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LITERATURE REVIEW ON PITCH UTILIZATION AND TECHNICAL PROPOSAL FOR A CATALYTIC PITCH CONVERSION SYSTEM

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SECTION 1.0 - SUMMARY

1.0 SUMMARY

A literature review of processes that are at or near commercial operation for the consumption or conversion of petroleum pitch (525°C+) has been completed as Task 1 of this study. Since CANMET did not restrict the type of pitch, a wide range of sources from conventional crude oils through heavy oils and bitumen processing to coal liquefaction were considered for the pitch. Five major types of pitch conversion process were reviewed: non-catalytic and catalytic pyrolysis, hydrogen addition, non-catalytic and catalytic gasification. A review of the basic research and proposed reaction mechanisms was done for each major type of process prior to summarizing the specific processes. For each specific process a flow schematic, process description, product yields and properties have been developed. Comparative economic data could not be developed from the literature review since each case is on a different economic basis. Where available, the utility consumptions and a capital cost value were provided.

Non-catalytic pyrolysis processes are being widely used with a variety of pitch feeds. Exxon's Dual Gasification Flexicoking process, though non-catalytic, is very similar in overall concept to CANMET's pitch pyrolysis/gasification process. Recent economic studies related to Athabasca bitumen or heavy oil processing have shown an advantage for hydrogen addition processes over non-catalytic pyrolysis processes.

Catalytic pyrolysis processes have not been widely applied to heavy pitch conversion because of problems with impurities and coke depositing on the catalyst. CANMET has not yet done any testing of a pyrolysis catalyst that would be less susceptible to these problems.

Non-catalytic gasification is well proven commercially and several process licensors are developing catalytic gasification processes using alkali metal catalysts. The gasification catalyst testing reported by CANMET does not have any novel aspects since an alkali metal carbonate was used.

A wide range of sources was reviewed during Task 2 of the study, to develop the pitch properties defined by CANMET for the full spectrum of pitch feeds. Many of the required properties are not normally measured and process licensors were contacted directly for data to supplement the literature search. All the available chemical and physical property data have been provided in tabular form.

A conceptual evaluation of a continuous laboratory test unit for the catalytic pyrolysis and gasification reactions was completed as Task 3 of the study. Since sufficient laboratory data are not available for an engineering design, discussions of flowsheet concepts and recommendations of additional test work are given for use in the subsequent engineering design of the laboratory test unit. A review of other work with sticky feeds has shown that agglomeration can be avoided in a fluidized bed by operating with a high ratio of solids to sticky substance. As a result, fluidized bed reactors are recommended for both the pyrolysis and gasification test unit reactors. A riser pyrolysis reactor was considered but was rejected as infeasible with the 30 minute solids residence time specified by CANMET.

In the past, CANMET has experienced problems with a fluidized bed pyrolysis test reactor which was subject to agglomeration. The overall test unit concept that is proposed is based on fluidized beds with design concepts and operating guidelines to minimize agglomeration in the pyrolysis reactor. The development of basic catalyst fluidization properties must be done by CANMET before the design of the test unit can be completed.

A heat balance calculation at a high catalyst:pitch ratio showed that CANMET's concept of integrating the pyrolysis and gasification units in the same manner as a fluid catalytic cracker may require the removal of excess heat from the hot catalyst leaving the gasifier.

The unique aspect of CANMET'S pitch pyrolysis/gasification process is the use of a bifunctional catalyst with active components for both the pyrolysis and gasification reactions. CANMET has not yet tested any bifunctional catalysts and it is recommended that this concept be demonstrated on a batch basis before any further work is done on the continuous laboratory test unit. The work reported by CANMET on separate pyrolysis and gasification has used catalysts that may be difficult to use in a bifunctional mode.

When the bifunctional catalyst concept has been demonstrated, it is recommended that CANMET consider collaborating with one of the Canadian research groups developing novel pyrolysis reactors.

1.1 SOMMAIRE

Un examen de la documentation des procédés qui sont en opération commerciale ou en voie de le devenir, pour la consommation ou la conversion de goudron de pétrole (525°C+) a été complété comme tâche No. 1 de cette étude. Étant donné que CANMET n'a pas mis de restriction sur le type de goudron, une large gamme de sources a été considérée pour le goudron à partir des pétroles bruts conventionnels en passant par les huiles lourdes et les procédés de bitume jusqu'à la liquéfaction du charbon. Cinq types majeurs de procédé de conversion ont été examinés: pyrolyse non catalytique et catalytique, addition d'hydrogène, gazification non catalytique et catalytique. Un examen de la recherche fondamentale et des mécanismes de réaction proposés a été effectué pour chaque type principal de procédé avant de résumer les procédés spécifiques. Pour chaque procédé spécifique un schéma de débit, une description du procédé, les rendements et propriétés des produits ont été développés. Des données économiques comparatives n'on pu être développées à partir de l'examen de la documentation étant donné que chaque cas relève d'une base économique différente. Lorsque disponibles, les consommations et une valeur du capital investi ont été fournies.

Les procédés de pyrolyse non catalytique sont largement utilisés pour une variété d'alimentation de goudron. Le procédé de gazification double "Flexicoking" de Exxon, bien que non catalytique, est très similaire dans sa conception d'ensemble au procédé de pyrolyse/gazification du goudron de CANMET. Des études économiques récentes relatives au procédé du bitume Athabasca ou de l'huile lourde ont montré un avantage pour les procédés d'addition d'hydrogène sur les procédés de pyrolyse non catalytiques.

L'application des procédés de pyrolyse catalytique pour la conversion du goudron lourd n'est pas très répandue à cause de problèmes provenant des impuretés et des dépôts de coke sur le catalyseur. Jusqu'à présent CANMET n'a procédé à aucun essai d'un catalyseur de pyrolyse qui serait moins affecté par ces problèmes.

La gazification non-catalytique est commercialement bien éprouvée et plusieurs détenteurs de permis de procédé développent des procédés de gazification catalytique utilisant des catalyseurs de métal alkali. L'essai de catalyseur de gazification rapporté par CANMET ne présente aucun aspect nouveau étant donné qu'un carbonate de métal alkali a été utilisé.

De nombreuses sources ont été examinées durant la tâche No. 2 de l'étude dans le but de développer les propriétés de goudron définies par CANMET pour la gamme complète d'alimentation de goudron. Plusieurs des propriétés requises ne sont pas normalement mesurées et les détenteurs de permis du procédé ont été contactés directement pour obtenir les données destinées à appuyer la recherche de documentation. Toutes les données disponibles des propriétés chimiques et physiques ont été fournies sous forme de tableau.

Une évaluation du concept d'une unité d'essai de laboratoire en continu pour les réactions de pyrolyse catalytique et de gazification a été complétée comme tâche No. 3 de l'étude. Étant donné que des données suffisantes de laboratoire ne sont pas disponibles pour une conception d'ingénierie, des discussions sur les schémas de procédés et des recommandations pour des travaux d'essais additionnels sont donnés pour le design subséquent de l'unité d'essai de laboratoire. Un examen d'autres travaux sur des alimentations collantes a montré qu'une agglomération peut être évitée dans un lit fluidisé en opérant avec un haut rapport de solides sur la substance collante. Il en résulte que des réacteurs à lit fluidisé sont recommandés pour les unités d'essai de pyrolyse et de gazification. Un réacteur d'élévation de la pyrolyse a été considéré mais fût rejeté comme n'étant pas approprié à cause du temps de résidence des solides de 30 minutes spécifié par CANMET.

Dans le passé, CANMET a eu des problèmes avec un réacteur d'essai de pyrolyse pour lit fluidisé soumis à l'agglomération. Le concept d'ensemble de l'unité d'essai qui est proposé est basé sur des lits fluidisés avec des concepts d'agencement et des données générales d'opération propres à minimiser l'agglomération dans le réacteur de pyrolyse. Le développement des propriétés de fluidisation du catalyseur de base doit être effectué par CANMET avant que la conception de l'unité d'essai puisse être complétée.

Un calcul de la balance de chaleur pour un haut rapport catalyseur:goudron a montré que le concept de CANMET intégrant les unités de pyrolyse et de gazification de la même manière qu'un craqueur de catalyseur fluide peut exiger l'évacuation de l'excès de chaleur du catalyseur chaud qui quitte le gazificateur.

L'aspect unique du procédé de pyrolyse/gazification de goudron de CANMET consiste en l'utilisation d'un catalyseur bifonctionnel avec des composants actifs pour les réactions de pyrolyse et de gazification. CANMET n'a pas encore procédé aux essais des catalyseurs bifonctionnels et il est recommandé que ce concept soit démontré sur une base de quantités séparées avant de procéder à d'autres travaux sur une unité d'essai de laboratoire continue. Les travaux rapportés par CANMET sur la gazification et la pyrolyse séparées sont basés sur l'utilisation de catalyseurs qui peuvent être difficiles à utiliser dans un mode bifonctionnel.

Lorsque le concept de catalyseur bifonctionnel aura été démontré, il est recommandé que CANMET considère de collaborer avec un des groupes de recherche canadiens développant les nouveaux réacteurs de pyrolyse.

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SECTION 2.0 - INTRODUCTION

2.0 INTRODUCTION

Pitch, or vacuum residuum, boiling above 525°C is produced during refining of conventional crude oils and upgrading of heavy oils and bitumen. The concentrations of impurities such as sulphur, nitrogen and metals are higher in the pitch than in the original oil. The direct uses for this pitch, and hence its marketability, become more limited as these impurity levels increase. This problem is particularly severe with pitch produced from processing heavy conventional oils or upgrading heavy oils and bitumen. There is, therefore, need to establish technologies for the conversion of pitch into usable products.

CANMET has been developing a pitch pyrolysis/gasification process since 1977. The pyrolysis reaction produces liquid transportation fuel products from the pitch and the gasification reaction produces synthesis gas from the coke char that is formed during pyrolysis. A series of batch microbalance tests has been done at CANMET and a patent obtained for the process. The unique aspect of CANMET's pyrolysis/gasification process is the use of a bifunctional catalyst which has active components for catalyzing both the pyrolysis and gasification reactions.

A fluidized bed laboratory test unit was constructed by CANMET for testing the pyrolysis process with gamma alumina catalyst. The fluidized bed was never successfully operated as reactor plugging problems were experienced with the viscous, sticky pitch feed. These problems must be resolved if the pyrolysis/gasification process is to be developed further.

The object of this study, therefore, is to provide:

- data base compilations of pitch conversion processes and pitch properties for CANMET's use in determining both potential uses for future Canadian pitch production and the potential application for the pyrolysis/gasification process, and

- a conceptual evaluation of a laboratory test unit for the further development of the catalytic pyrolysis/gasification process. The conceptual evaluation in this report is for use in the subsequent engineering design of the laboratory test unit.

The scope of work for the study is defined in Hatch Associates' proposal to CANMET (1).

The work in Task 1 is reported in Section 3.0. This is the result of a literature search to define the processes that are now being used commercially to produce usable products from pitch. Some development processes are included that are similar in concept to the process CANMET is developing. The processes reviewed cover the production of:

- asphalt
- energy from pitch combustion
- liquid and gaseous products from catalytic and non-catalytic pyrolysis both with and without hydrogen addition
- gaseous products from catalytic and non-catalytic gasification
- coke.

Task 2 was a literature search to compile physical and chemical properties of pitches. The results are tabulated in Section 4.0. Properties are given for pitches from a wide variety of processes and crudes since CANMET did not restrict the pitch source. The properties tabulated are those that were identified by CANMET as of most interest.

The conceptual laboratory test unit evaluation was Task 3 and the results are in Section 5.0. The evaluation has been done using process guidelines provided by CANMET and has reviewed other fluidized bed work that used viscous, sticky feeds. The object of Task 3 was to provide ideas and a conceptual evaluation for a laboratory test unit that could be used in the subsequent engineering design of the unit. A block flow diagram was developed for the test unit but detailed drawings and calculations were not part of the scope of work.

Standard SI units are used throughout the report.

SECTION 3.0 - METHODS OF PITCH CONSUMPTION

3.0 METHODS OF PITCH CONSUMPTION

This section presents the results of a literature search to define the processes that are now being used commercially to produce usable products from pitch. The type of pitch was not restricted by CANMET and, depending on the process, could be the residuum boiling above 525°C from:

- distillation of conventional and heavy crude oils, oil sands bitumen or shale oil

- upgrading processes treating the above pitches from distillation

- fluid catalytic cracking

- coal liquefaction processes

- ethylene production from liquid hydrocarbon feeds.

The review is limited to processes at or near commercial operation. Some development processes that are similar in concept to the process CANMET is developing are also included. An overview listing processes in the development stage has been given by Schuetze and Hofmann (2).

The literature review is based primarily on data base searches from Applied Science and Technology Index, Engineering Index, Alberta Oil Sands Index, Alberta Coal Technology Index and an Asphaltene Bibliography prepared by the University of Calgary (3). The objective of the literature search was to obtain sufficient reference material to define each of the processes under consideration. This objective was achieved but because this work had a defined budget, the literature review:

- could not be a fully exhaustive compilation of all the references available on each subject.

- had no date constraints imposed on the articles reviewed.

The literature review was considered complete when sufficient information was available for each of the pitch processing areas to define:

- a description of the process
- reaction mechanisms, where applicable
- products from the process and their properties
- production cost and current product values.

These are presented in the following sections for each process covered in the different processing areas. The major pitch processing areas that are reviewed are:

- asphalt production (Section 3.1)
- direct combustion (Section 3.2)
- non-catalytic pyrolysis (Section 3.3.1)
- catalytic pyrolysis (Section 3.3.2)
- hydrogen addition (Section 3.3.3)
- non-catalytic gasification (Section 3.4.1)
- catalytic gasification (Section 3.4.2)
- coke and electrode binder production (Section 3.5)

The most difficult topic to address on a consistent basis was the definition of production costs and current product values, particularly the production costs. This is because in many cases production cost data are not given or when they are given each process licensor uses a different basis and many do not apply to Canadian conditions. These costs can also vary significantly, depending on the process, with the type of pitch feed, the degree of conversion and the required product properties. As a result, defined production costs cannot be given for many of the processes. More useful data for cost evaluation are the utility and consumable requirements and, when published, these are presented in the following sections. These values can then be used for economic evaluation by each reader under his own economic conditions.

3.1 Asphalt Production From Pitch

Asphalt is readily produced from pitch by several different methods to give a very wide range of product properties. The chemical composition of the crude oil determines the asphalt yield, quality and the processing conditions required for its production. With an increase in asphaltene and resin substances and asphaltene/resin ratio, and a decrease in paraffins in the oil, the asphalt yield increases and the processing conditions become milder. The range of processing conditions is further increased by the wide variety of product asphalt specifications to suit the many uses of asphalt. Because of this wide range of feed and product properties and, therefore, operating conditions, there are no standard economics or specific utility consumptions for asphalt production. This is shown in Table 3.1 by data from Snamprogetti (4) of utility requirements to produce various penetration grade asphalts from Kuwait vacuum residuum by air blowing. As a result, production cost data for asphalt are not given in this section.

Many properties and uses for asphalt are published (5) and the key points are presented below. A presentation of detailed properties for the many grades of asphalt is beyond the scope of this work and asphalt references such as (5, 6, 7) should be consulted. Product values for all asphalt grades cannot be given, but values from Chemical Marketing Reporter (8) converted to Canadian dollars are:

Petroleum cutback asphalt	$0.31/L
Emulsion asphalt	$0.25/L
Steam refined 40-300 penetration asphalt	$ 255/t
Steep roofing grade asphalt	$ 265/t

(a) Straight Asphalt

Pitch can be used directly as asphalt with its most common application in pavements. These straight reduced asphalts

TABLE 3.1

ASPHALT BLOWING UTILITY REQUIREMENTS

Penetration Grade (25°C) Asphalt Produced	80/100	60/70	40/50	20/30
Utilities/t Kuwait 550°C + Pitch Feed				
Air, Nm^3	27	42	62	96
Electricity, kWh	4	7	10	15
Boiler Feed Water (BFW), t/h	160	160	160	160
Fuel, MJ	25	42	63	84
Steam, Low Pressure, kg	(154)	(154)	(154)	(154)

(   ) Amount produced

serve as binders in paving mixes and as bases in liquid asphalts used in seal coatings, surface treatments, road mixes and soil stabilizers. The atmospheric pitch (long residuum) from a crude oil containing 30 percent or more asphalt can be used directly as a road asphalt. For crude oils with 15-30 percent asphalt, the short residuum produced by vacuum distillation is used. Asphalt production by distillation does not change the chemical nature of the asphalt. The softening point and penetration of the asphalt vary with the distillation cut point for a given oil and vary widely for different oils at a given distillation cut point.

CANMET has determined that hydrocracked pitch residues from the CANMET process can be used in road asphalt production (9).

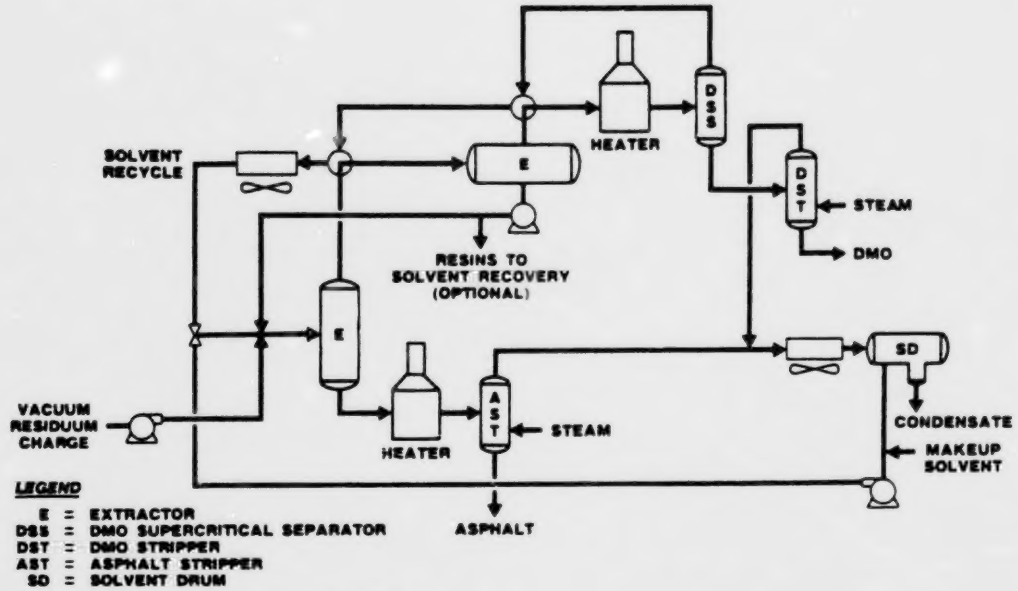
(b) Solvent Deasphalting

Solvent deasphalting is used to produce asphalt from crude oils with a low asphalt content of less than 15%. With higher asphalt content crude oils, solvent deasphalting produces a hard asphalt that can be blended as a hardening component with softer asphalts. The most common solvent used is propane but butane and pentane have been used as well with the heavier solvents producing harder asphalt products. The basic process has been widely reported (10-12) and a recent development uses supercritical conditions for solvent recovery to reduce the utility requirements and capital cost (12-15). A simplified solvent deasphalting flowsheet is in Figure 3.1 (12). The process often uses counter-current liquid-liquid extraction with charge stock, normally atmospheric residuum, introduced near the top of the extraction tower and the liquid solvent near the bottom with solvent: oil ratios ranging from 4:1 to 10:1. As shown in Figure 3.1, the solvent and oil can also be mixed prior to the extractor. A deasphalted oil-solvent solution is withdrawn overhead and the asphalt from the bottom. Each is then stripped of solvent. As with distillation, solvent deasphalting is a physical separation process and no chemical changes occur that would affect the quantity or properties of the asphaltenes. The oils and some of the resins in the feed are recovered with the overhead solvent phase while the remaining resins and the asphaltenes are produced with the asphalt product. The split in these recovered components depends on the solvent with heavier solvents recovering more resins in the overhead product and leaving a heavier asphalt product. The asphalt properties produced by solvent

FIGURE 3.1

SOLVENT DEASPHALTING PROCESS FLOWSHEET

(With Supercritical Solvent Recovery)


HEATER
DSS
SOLVENT RECYCLE
E
DST
STEAM
DMO
RESINS TO SOLVENT RECOVERY (OPTIONAL)
E
SD
VACUUM RESIDUUM CHARGE
HEATER
AST
STEAM
CONDENSATE
MAKEUP SOLVENT
ASPHALT

LEGEND

E = EXTRACTOR
DSS = DMO SUPERCRITICAL SEPARATOR
DST = DMO STRIPPER
AST = ASPHALT STRIPPER
SD = SOLVENT DRUM

DMO = DEASPHALTED OIL PRODUCT

deasphalting can be similar to those from direct distillation or harder depending on the solvent and operating conditions used. Asphalt produced from this process is normally blended with other residues for making paving asphalt but is also used in fesco board manufacture and self-sealing roofing shingle adhesive. Because of its high softening point, it acts as a hardening component and can eliminate need for oxygen blowing. Since they contain little or no paraffin wax but more organic acids than straight run asphalts, they are more suitable for asphaltic emulsions (11).

The properties of paving grade asphalts made by three different processes from in-situ retorted bitumen near Vernal, Utah have been reported (16). The asphalts were produced by vacuum distillation, flash vapourization and solvent extraction. They were found to have no striking property differences compared to paving grade asphalts from conventional petroleum.

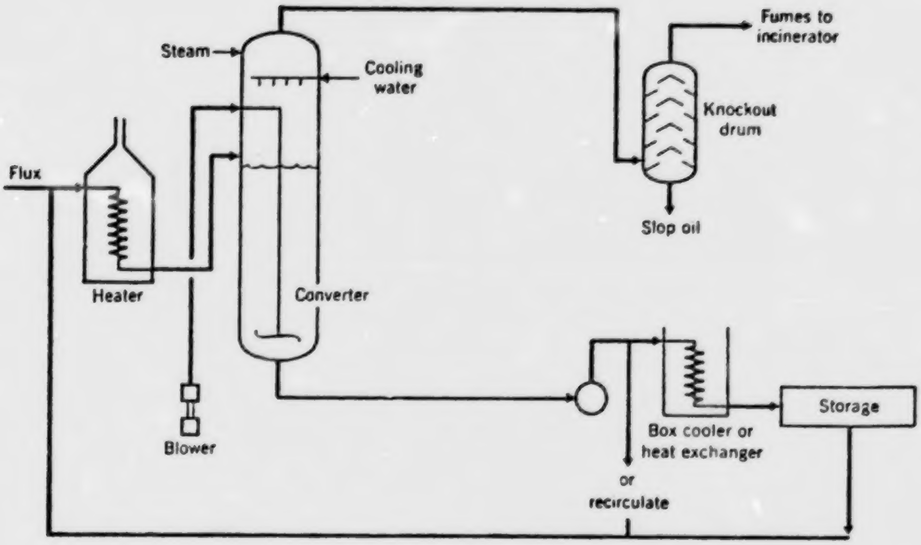
(c) Air Blowing

Air blowing is a process in which an asphalt stock is converted to a harder product by reaction with oxygen in air at 200-275°C in either a batch or continuous reactor. Air blown asphalts are more resistant to weather and changes in temperature than the types mentioned above and with added fillers, polymers, solvents and in water emulsions provide products for many applications in the roofing industry. Other uses include laminants, pipeline coatings, waterproofings, potting compounds and joint fillers (5). The continuous process predominates now because it has the advantages of lower equipment and maintenance costs for the same production capacity, shorter blowing times, less preheat requirement, better process control, lower blowing losses and lower operating labour requirement. The continuous process has a particular advantage when several asphalt grades are to be made from one feed. Two major licensors of the continuous process are Snamprogetti (4) and BP (4).

A flow sheet of the continuous blowing process is in Figure 3.2 (5). Where the feed is coming directly from a vacuum distillation unit, the heater would be replaced by a cooler to control the feed temperature at about 140-190°C. The exothermic reactions raise the product asphalt temperature to about 260-290°C and the overhead vapour to about 200°C. Cooling

FIGURE 3.2

CONTINUOUS AIR BLOWING PROCESS FLOWSHEET


Steam
Cooling water
Fumes to incinerator
Knockout drum
Flux
Slop oil
Heater
Converter
Blower
Storage
Box cooler or heat exchanger
or recirculate

water is added directly to control the reactor temperature. The overhead vapour is burned with supplemental fuel in an incinerator. The blowing reactor is an open cylindrical vessel with air manifolds near the bottom (5, 17-18). Catalysts have been tried to reduce the blowing time and change the softening point - penetration relationship of the asphalt product. Catalysts used have been copper sulphate, zinc chloride, ferric chloride, aluminum chloride, phosphorus pentoxide and others (5). Since they are consumed during the reaction, they are not true catalysts. Corbett (19) used phosphorus pentoxide and ferric chloride and found higher penetration at a given softening point compared to a straight air blown asphalt.

The air blowing reactions involve dehydrogenation and polymerization with the oxygen not retained in the asphalt product except in a minor amount. The oxygen combines with hydrogen in the asphalt to evolve water vapour and leave unsaturated compounds for cross-linking reactions. Corbett (19) found that the reaction mechanism involved naphthene-aromatics being converted to polar-aromatics which in turn were converted to asphaltenes. The saturates showed little or no change during the blowing conversion. Results from an Arkansas crude (5) show that the increase in asphaltene fractions is almost entirely at the expense of resin fractions with only a small oil conversion. With Athabasca bitumen (20), it was found that the increase in asphaltene was at the expense of the oil fraction with the resins almost unchanged. A correlation has been developed (21) that predicts the rate of asphaltene formation during air blowing based on the compounds in the feedstock that are capable of forming asphaltenes, namely monocyclic and bicyclic aromatics, benzene eluted resins and alcohol/benzene eluted resins. The paraffinic/naphthenic hydrocarbons did not react to form asphaltenes. This work supports the results of references (5) and (19) that the resin fraction provides the compounds that react to asphaltenes during air blowing.

Asphalt has been produced by air blowing both whole and vacuum reduced Athabasca bitumen (20). The product from air blowing of whole bitumen was an asphalt comparable to commercial asphalts while the asphalt from air blowing of vacuum residue had higher softening points and lower penetrations than commercial asphalts. Other investigators (22) found that specification paving asphalts could be produced from oxidation of heavy crude oil distillation residues.

(d) Other Asphalts

Thermal asphalts are produced from the residues remaining after thermal cracking processes such as discussed in Section 3.3. They have high specific gravity, low viscosity, high temperature susceptibility and contain cokelike bodies (carbenes). They are useful as binders and as saturants for fibreboards, brick-finish siding and fibre soil pipes (5).

In addition to the single source asphalts discussed above, there is a whole range of blended asphalts. The blending may involve two grades of asphalt or an asphalt blended with various petroleum distillate fractions, from naphtha to gas oil, to form cutback asphalt with different curing properties. Blending 25-30 mass percent hydrocracked pitch residue with a 150-200 penetration road asphalt cement was found to produce a roofing asphalt directly without blowing (9). Asphalt emulsions with the asphalt dispersed in a continuous water phase are also made for a wide variety of uses. A review of these asphalts is beyond the scope of this study and reference 5 should be consulted for more details.

(e) Summary

As shown above, most of the pitches considered in this study could be produced as asphalt or blended with asphalt, even the pitch residues from bitumen and heavy oil processing and upgrading. The production of pitches, however, is in excess of the available asphalt product market and other uses must be found for consuming the majority of the pitch production. These are discussed in the following sections.

3.2 Direct Combustion of Pitch

When considering the direct combustion of pitch, the concentrations of impurities such as sulphur, nitrogen and metals become a concern along with properties such as viscosity and C/H ratio. The areas that must be addressed are (23):

- high viscosity - storage, transport, combustibility

- high C/H ratio - combustibility, particulate emissions

- high sulphur content - SO_x emissions
- high nitrogen content - NO_x emissions
- high metals content - high temperature corrosion
- ash content - ash disposal.

The detailed pitch properties in Section 4.0 will give an indication of the relative problems with different pitches. In general, pitch sources should be ranked for direct combustion as follows, proceeding from most desirable to least desirable: sweet conventional crude oil, sour conventional crude oil, heavy oil, oil sands bitumen, residue from upgrading heavy oil or oil sands bitumen. With the least desirable pitches all six of the problem areas listed above would have to be considered. Other possible pitch fuel sources include shale oil, coal liquefaction and coal tar. Shale oil combustion tests (24) have shown that the high nitrogen content of about 1.8 mass percent in whole crude shale oil results in high NO_x emissions and is the main problem when burning this fuel. Raw coal liquids (25) have high C/H ratios and nitrogen levels which may require burner and furnace redesign or hydrotreatment to overcome. Testing with coal tar (26) found it to be very viscous and unstable to the extent it could not be stored and burned as produced without additional hydrotreating.

The incentive for considering direct pitch combustion is cost since it is usually a residual refinery product that may have no other use when it cannot be produced as asphalt. The value given to pitch as fuel is the value of the alternate fuel, such as natural gas, that is displaced less the incremental capital and operating costs involved in pitch combustion, such as for emission control or viscosity reduction. Lutz (27) has calculated the fuel value of high sulphur (7.6 mass percent) pitch with flue gas desulphurization compared to the use of natural gas priced at \$3.79/GJ. High ash pitch was worth \$0.39/GJ in Venezuela or nil at Fort McMurray while low ash pitch was worth \$1.88/GJ in Venezuela or \$1.26/GJ in Fort McMurray. Unless these pitches could realize a greater value in another application, their use as fuel would be economically justified.

With the more favoured pitch fuel sources, sweet and sour conventional crude oils, the main problem with pitch combustion has been viscosity. This has been overcome by blending the pitch with a lighter hydrocarbon or cutter stock to produce the widely used No. 6 fuel oil. This blending is discussed in Section 3.2.1. With pitches from the less desirable feed sources, a large amount of cutter stock would be required and alternative combustion methods are being developed. RAROP in Japan (23) has been developing, on a pilot plant scale, all aspects of combustion, boiler design and emission control for the combustion of undiluted liquid pitch. Also in Japan, pitch from the Eureka process has been solidified, pulverized and burned in an existing boiler with no auxiliary fuel (28). In 1983, a boiler designed to generate 130 t/h of steam from fuel oil was successfully converted to pulverized solid Eureka pitch combustion. UOP (15) has reported the commercial operation of a pitch flaker in Texas. Compared to delayed coke as a fuel, UOP shows that flaked pitch has a higher heating value requiring less fuel for a given duty, a higher volatile matter content making it easier to burn, and a higher Hardgrove grindability index requiring less grinder horsepower. A third approach, that has been successfully tested by Kerr-McGee, is the combustion of an emulsion of pitch in water (29). They found the emulsion could be handled in conventional systems designed for heavy fuel oil with only burner modifications possibly needed.

Sulphur content in fuel oil has become more of a concern recently but this has usually been resolved by using enough low sulphur fuel to meet the overall emission specification. Pitches from the heavier, less desirable feed sources have such a high sulphur content that they would require sulphur capture, as discussed in Section 3.2.2, if they were to be used as fuels.

3.2.1 Heavy Fuel Oil Blending

The most common use for pitch has been as heavy or No. 6 fuel oil. The requirements for this product are governed by Canadian General Standards Board specification CAN2-3.2-M81 (formerly 3-GP-2) and by ASTM Specification D396. These specifications set few requirements for No. 6 fuel oil with only viscosity, flash point and water and sediment content being limited as follows:

Viscosity @ 50°C	92 min to 638 max mm^2/s
Flash point	60°C min
Water and sediment	2 mass percent max

Although not a requirement of the specification, the sulphur content is usually limited by sulphur oxide emission limitations where there is no SO_2 recovery so that a typical high sulphur No. 6 fuel oil would contain about 2.5 mass percent sulphur and a typical low sulphur No. 6 fuel oil about 1.25 mass percent sulphur. As the pitch properties in Section 4.0 show, there are few pitches with a sulphur level this low. The most common practice is to either use some pitch from sweet crude oil to reduce the sulphur level or to blend the pitch with a lighter distillate hydrocarbon or cutter stock to reduce both the sulphur level and viscosity of the fuel oil. A distillate cutter stock with a 204°C to 343°C boiling range is often used. Light cycle oil from fluid catalytic cracking is preferred because it has lower viscosity than a straight run cut of the same boiling range and would require hydrotreating if it were blended with lighter products. The value of the light cycle oil is downgraded when blended in No. 6 fuel oil since it could also be hydrotreated and blended in No. 2 fuel oil. Current (mid-1985) prices of 1 wt% sulphur No. 6 fuel oil are \$195/m^3 while 0.2 mass percent No. 2 fuel oil is \$248/m^3 (30) which shows that the use of cutter stock would become uneconomic with most high sulphur pitches produced from sour conventional crude oil, heavy oil, oil sands bitumen and residues from upgrading heavy oil or oil sands bitumen. If Lutz's example (27) is used, one volume of the 7.6 mass percent sulphur pitch would have to be blended with about 9 volumes of 0.2 mass percent sulphur cutter stock to produce a 1 mass percent low sulphur fuel oil. With the low sulphur fuel and cutter stock valued as above, the pitch feed would be given a negative value. An economic limit is, therefore, reached with high sulphur pitches where direct combustion in a furnace with flue gas desulphurization or in a fluidized bed boiler as reviewed in Section 3.2.2 is less costly than blending to reduce the sulphur content of the fuel oil.

3.2.2 Combustion With Sulphur Capture

There have been numerous articles published on the recovery of sulphur compounds from the combustion of high sulphur fuels. The purpose of this section is not to present a detailed review of all these references but to give an overview of the available technologies. Both flue gas desulphurization and fluidized bed combustion have been proven commercially and are discussed below. There are other new technologies being developed such as limestone injected burners which add the sorbent in the burner for direct SO_2 capture (31, 32). These newer development processes are not covered since they are not commercially proven.

Since vanadium catalyzes the oxidation of sulphur dioxide to sulphur trioxide, the sulphur capture system for direct combustion of lower quality pitches must also include allowance for SO_3 recovery and/or sulphuric acid mist elimination.

(a) Flue Gas Desulphurization

There are many flue gas desulphurization articles available including books that review the current technologies (33) and articles on individual processes such as lime-limestone wet scrubbing (34, 35), dry scrubbing (36, 37), magnesium oxide (38) and Wellman-Lord (39). There are two main process types:

(i) throwaway which includes lime-limestone wet and dry scrubbing producing a waste sludge or gypsum product.

(ii) regenerative which recover the sulphur in elemental form or as sulphuric acid and recycle the sorbent back to the absorber.

The best technical and economic evaluation of the processes in these two main categories was recently published by the Electric Power Research Institute (40). The study evaluated the recovery of sulphur from combustion of a high sulphur (4 mass percent) bituminous coal but similar results should be found for sulphur recovery from combustion of a high sulphur pitch. They evaluated both proven and developing processes in the throwaway and regenerative categories on as close to a consistent basis as possible. The study found the throwaway processes were less expensive than the regenerative processes.

The levelized incremental electricity costs required to pay for some of the proven FGD systems studied are listed below in mills/kWh where 1 mill is U.S. $0.001.

	Incremental Electricity Cost, Mills/kWh
Throwaway processes	
Chiyoda Thoroughbred-121	14
Limestone dual alkali	16
Lime dual alkali	17
Limestone slurry	18
Lime slurry	20
Regenerative processes	
Magnesium oxide with sulphuric acid by-product	19
Wellman-Lord with sulphur by-product	26
Aqueous carbonate with sulphur by-product	30

The magnesium oxide cost includes a larger credit for sulphuric acid production than the sulphur product credit of the other two regenerative processes. Since large quantities of sulphuric acid cannot be economically stored, it must be sold as produced at current market conditions and a large product credit may not always be realized. Because sulphur can be stored in solid form, its sale can be less susceptible to market changes.

The economic evaluation in the EPRI study shows that the limestone or lime scrubbing processes producing a waste landfill product are less expensive to build and operate than the regenerative processes producing a sulphur or sulphuric acid product. Because of this cost advantage and reliability concerns with the more complex regenerative processes, the throwaway processes accounted for 94 percent of the installed FGD controlled generating capacity and all of the 98 new units under construction or planned by U.S. utilities as of September, 1983 (41).

While the majority of the commercial FGD experience has been with flue gas from coal combustion, there have been some systems, particularly Wellman-Lord, associated with heavy oil combustion.

It is known that the base case process configuration being developed by Canstar Oil Sands Ltd. included the direct combustion of Eureka process pitch with a limestone FGD scrubbing system producing a throwaway landfill. Eureka has reported the commercial demonstration of pulverized solid pitch combustion with flue gas desulphurization in a boiler producing 130 t/h of steam (28). Eureka's economic evaluation shows an incentive to burn pitch rather than natural gas. They calculated a cost of upgrading 1590 m^3/d Cold Lake bitumen with natural gas as fuel at $23.30 U.S. per m^3 of feed compared to $19.06 U.S. per m^3 of feed when all the product pitch was burned with flue gas scrubbing and the excess thermal energy was used to generate export steam for injection into the formation. If there had not been a credit for steam export, the combustion of natural gas would have been preferred. The results presented by Lutz (27) at the beginning of Section 3.2 showed an incentive to burn pitch with FGD rather than natural gas for all cases except a high ash pitch in Fort McMurray. There may, therefore, be an economic incentive to burn pitch with flue gas desulphurization in commercially proven systems given the right project conditions.

(b) Fluidized Bed Boiler

The application of fluidized bed boilers has advanced very rapidly since the first commercial unit in North America began operation in 1979. There are a number of industrial applications and utilities are building demonstration scale (110-160 MW) plants. The advantages of the system leading to its rapid development include:

- direct sulphur capture in the boiler producing a dry waste product.
- low temperature combustion (790-950°C) so that fixation of atmospheric nitrogen as NO_x is much reduced. The low temperature also lessens volatilization of metals such as sodium and potassium which reduces deposits on superheaters and reheaters. Slagging does not occur at these temperatures as in a pulverized boiler at 1370°C which gives flexibility to burn low grade fuels.
- high fuel efficiency, with carbon burnup as high as 99.9 percent, can be achieved because of the turbulent mixing conditions.

- high heat transfer rates result from the effect of the solid particles.

- high volumetric heat release rates of up to 25 times the rate in a pulverized coal boiler.

- almost any type of combustible material may be burned in a fluidized bed combustor giving the operator wide flexibility in fuel purchases.

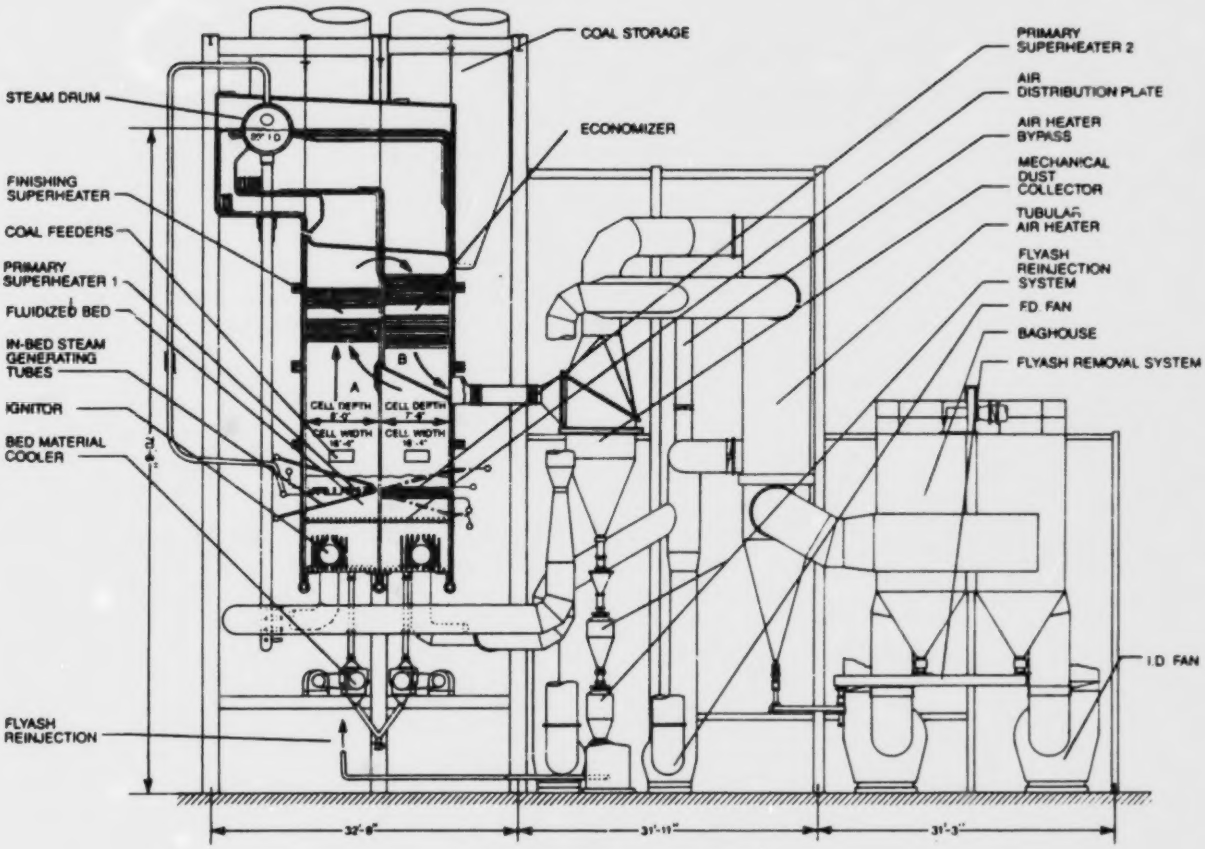
The three main types of systems that have been developed are atmospheric fluidized bed (AFB), pressurized fluidized bed (PFB) and circulating fluidized bed (CFB). Reviews of the vendors offering these systems and the commercial installations have been published (42, 43).

The AFB system is now the best developed and most widely used commercially. It will soon begin use with electric utilities in the United States as three plants of 110 to 160 MW size were ordered in 1984. The AFB is a simple concept with a bubbling bed of solids held on a perforated plate air distributor as shown in Figure 3.3 The bed is fluidized by flow of air slightly above atmospheric pressure at a rate low enough (below 3 m/s) to maintain the solid particles within the reactor. The fuel and sorbent materials, size of the air distributor perforations, fluidizing air velocity, and temperature can all be designed or controlled to achieve the required conditions. Steam is generated primarily in water tubes immersed in the fluidized bed. Depending on the design, the vertical tubes in the side waterwalls either generate steam or act as multiple downcomers to provide water for the in-bed tubes. Steam superheating usually is done in the freeboard above the bed with the feedwater preheater in some designs above the superheater. Cyclones recover unburned carbon from the flue gas for recycle to the bed to achieve a high carbon burnup efficiency.

The pressurized fluidized bed system operates at 10-15 atmospheres pressure and is being developed for use in an integrated gas turbine system for generation of steam and/or electricity (43, 44). It operates at relatively low fluidizing velocities so the solid particles remain in the reactor. The incentive for developing the PFB is the reduced volume which should allow boilers of up to 100-250 MW size, depending on the pressure, to be shop fabricated to reduce

FIGURE 3.3

ATMOSPHERIC FLUIDIZED BED BOILER


COAL STORAGE
PRIMARY SUPERHEATER 2
AIR DISTRIBUTION PLATE
STEAM DRUM
AIR HEATER BYPASS
ECONOMIZER
MECHANICAL DUST COLLECTOR
FINISHING SUPERHEATER
TUBULAR AIR HEATER
COAL FEEDERS
FLYASH REINJECTION SYSTEM
PRIMARY SUPERHEATER 1
FLUIDIZED BED
FD. FAN
BAGHOUSE
IN-BED STEAM GENERATING TUBES
FLYASH REMOVAL SYSTEM
IGNITOR
BED MATERIAL COOLER
A
B
CELL DEPTH
CELL DEPTH
CELL WIDTH 16'-4"
CELL WIDTH 16'-4"
I.D. FAN
FLYASH REINJECTION
32'-8"
31'-11"
31'-3"

Ref: Foster Wheeler Boiler Corp., Chem. Eng. Prog., pg. 36, January, 1984.

construction costs. Since the concept has not been commercialized, it will not be discussed further in this report.

Circulating fluidized systems have advanced very rapidly with eight units larger than 181,000 kg/h each being ordered recently in the United States. A schematic of a typical CFB is in Figure 3.4. This is the Battelle developed multi-solid fluidized bed (45) where an entrained bed of the fine ash and limestone particles, carried by high velocity gas flow, is superimposed on a fluidized dense bed of heavy particles that stay on the bottom of the combustor. The dense bed traps or slows down the fine particles increasing their residence time in the dense bed region. This increase in residence time can be up to an order of magnitude over a system with no dense bed. Intensive backmixing occurs in the dense bed region where most of the combustion reactions occur. The circulating entrained bed controls combustion temperature and carries a portion of the heat to a separate low velocity fluidized bed heat exchanger where the heat in the solids is recovered. Heat is also recovered from the flue gas by conventional techniques. The cooled entrained bed material is recycled to the dense bed to control the combustion temperature and to be heated again. This system is similar in general concept to other CFB processes being developed by Lurgi, Pyropower and Stone & Webster (46). The advantages of the CFB include:

- the combustion and heat transfer sections are separated, reducing boiler tube erosion and corrosion.

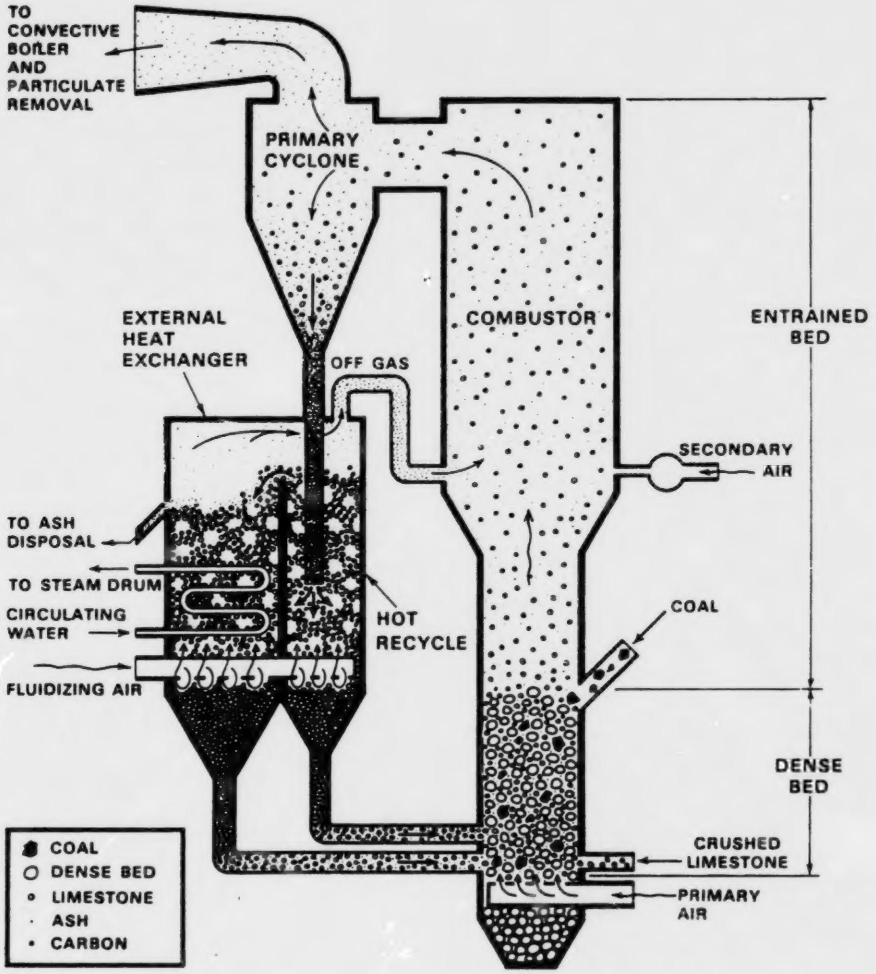
- the separate hot solids and hot gas heat exchange systems allows hot solids turndown to ratios of 6:1 or higher for rapid and controlled load following.

- recycling solids allows longer residence times, improving combustion efficiency at lower excess air levels. Fine limestone can be used allowing a reduction in Ca/S molar ratio to about 1.5, half the typical AFB value.

A 53 GJ/h Battelle multi-solids fluidized bed boiler has been installed by Conoco to generate 17 MPa steam for insitu heavy oil recovery in Texas (47). The unit has successfully burned coal and petroleum coke containing up to 7 mass percent sulphur. A Stone & Webster solids circulation boiler is being designed for Pemex to produce 110,000 kg/h of steam for

FIGURE 3.4

CIRCULATING FLUIDIZED BED BOILER


TO CONVECTIVE BOILER AND PARTICULATE REMOVAL
PRIMARY CYCLONE
EXTERNAL HEAT EXCHANGER
OFF GAS
COMBUSTOR
ENTRAINED BED
SECONDARY AIR
TO ASH DISPOSAL
TO STEAM DRUM
CIRCULATING WATER
FLUIDIZING AIR
HOT RECYCLE
COAL
DENSE BED
CRUSHED LIMESTONE
PRIMARY AIR
COAL
DENSE BED
LIMESTONE
ASH
CARBON

refinery use from solid asphaltene fuel. The Lurgi circulating boiler is scheduled to be the first North American utility application of CFB at New Brunswick Electric Power Commission. The planned fuel is high sulphur coal and oil shale.

None of the commercial experience to date with either AFB or CFB has reported the use of pitch fuels. However, since design for liquid wastes and sludges is claimed by many vendors, the use of pitch fuel in either liquid of solid form should be feasible.

There was not much economic data on fluidized bed boilers found during this literature survey. Preliminary estimates by Foster Wheeler show both the AFB capital cost and the resulting cost of electricity 12 percent below that of a conventional plant with FGD (48). The Electric Power Research Institute feels additional data from utility demonstration scale projects will allow accurate economics to be evaluated but expects electricity costs from fluidized bed plants to be about 10 percent less than from a conventional pulverized boiler system with fuel flexibility and cost the main factors (44). Lutz (27) presented cost data for fluid bed combustion of high sulphur, high ash, high vanadium pitch that shows the fluid bed is slightly better economically than a conventional boiler with FGD. The pitch value as fuel in the fluid bed when displacing a natural gas boiler with gas valued at \$3.79/GJ was calculated at \$1.05/GJ in Venezuela or \$0.57/GJ in Fort McMurray. These values compare to pitch values of \$0.39/GJ in Venezuela and no value in Fort McMurray for the comparable conventional boiler with FGD for a high sulphur, high ash pitch. These values indicate that fluidized bed boilers should be considered when the combustion of pitch is a viable option.

3.3 Production of Lighter Hydrocarbons from Pitch

The conversion of the asphaltenes is the main factor in producing lighter hydrocarbons from pitch. As traditionally measured, asphaltenes are a solubility class of compounds, namely those compounds insoluble in a saturated hydrocarbon solvent, usually n-pentane or n-heptane, but soluble in toluene. The molecular structure of asphaltene is very complex and, because of the large molecules involved, difficult to measure. In spite of this, asphaltene structure has been the subject of detailed study for over 40 years (49). A number of papers have been published that postulate asphaltene structures (50, 51) but a detailed review of this topic is beyond the scope of this work. A better understanding of the structure is important, however, because it will lead to more accurate prediction of processes and conditions needed to convert asphaltenes to lighter products. In very simplified form, the types of molecules involved in the pitch are shown in Figure 3.5 (52). The actual molecules are, of course, much larger. Speight (50) suggests that additional research needed to understand asphaltene structure should include study of:

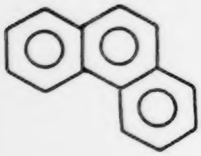
- skeletal structure
- the size of the polynuclear aromatic systems
- the internuclear bonds that need to be thermally or catalytically cleaved to produce lower molecular weight components
- the heteroatom types and difficulty of removal
- the metallic constituents and their occurrence in porphyrinic or non-porphyrinic locations
- the physicochemical relationships between the asphaltenes and other constituents of the oil.

Even without having detailed structural knowledge of the asphaltenes, there has been a great deal of process development, evaluation, and plant operation involving pitch conversion to lighter hydrocarbon products. The processes used may be divided into two broad categories, both of which increase the H/C ratio of the resulting liquid product:

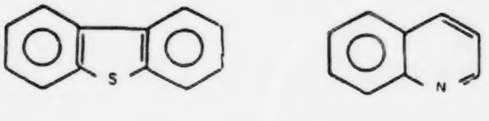
(i) carbon rejection which usually involves pyrolysis. Pyrolysis of waste streams such as municipal waste, tree bark, sewage sludge and waste polymers has been extensively reported. The review for this project has been limited, however, to catalytic and non-catalytic pyrolysis of the petroleum, bitumen, oil shale and coal based feeds covered by the scope of work.

FIGURE 3.5

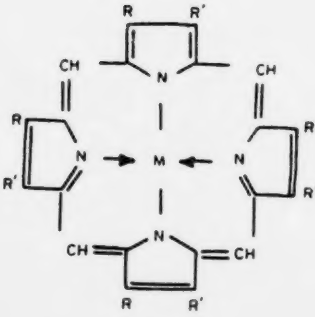
REPRESENTATIVE MOLECULAR TYPES IN PITCH



Polycyclic aromatic



Heteroatom cyclic compounds


R
R'
CH
N
CH
R
N
M
N
R
R'
R'
CH
N
CH
R
R'

Porphyrin

(ii) hydrogen addition which in most cases involves the use of a catalyst.

Lutz (27) has presented a plot of atmospheric pitch conversion versus process investment cost which is shown in Figure 3.6. The processes requiring least investment just separate the asphaltenes physically from the product oil. The slope change in the line occurs where asphaltene conversion to lighter products begins. The pyrolysis conversion processes are generally less costly than the hydrogen addition processes. Achieving low levels of unconverted pitch requires a large capital investment.

The hydrogen addition processes are not as well proven in commercial use as the pyrolysis processes but have made significant development progress in the last few years. The Alberta Oil Sands Technology and Research Authority (AOSTRA) has done a detailed evaluation of conversion processes and has a program underway aimed at demonstrating hydrogen addition processes with Athabasca bitumen feed.

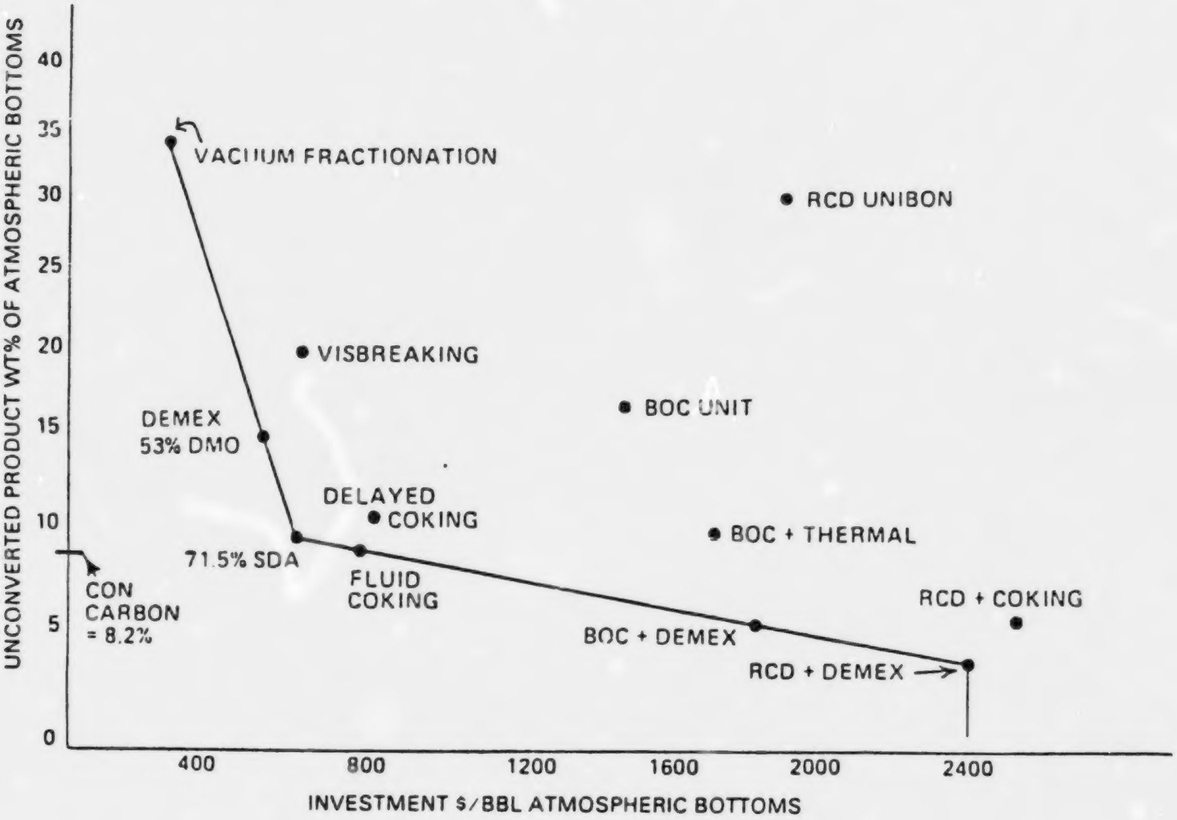
In spite of the advances in technology, no one process has emerged which is significantly better at pitch conversion than the others. Economic comparisons tend to show a spread of 2 or 3 percentage points in rate of return between different processes for a given application (53).

Bailey (54) has used data presented by Ring et al (55) to calculate an affordable price for crude which is the amount left over after deducting operating costs and capital charges from the product revenues. A high conversion H-Oil hydrocracking case with Athabasca bitumen had an affordable price for crude of $145/m^3 compared to only $115/m^3 for a coking case. Walker (56) showed data on a similar basis based on the AOSTRA study for a large scale 24,960 m^3/d Athabasca bitumen upgrader producing synthetic crude oil, and a small scale 3180 m^3/d Cold Lake bitumen upgrader producing pipelinable crude oil. With natural gas at $2.87/GJ, the affordable price for crude in the large case varied by only +5 percent for five hydrogen addition processes (including Donor Refined Bitumen) while the coking process was about 20 percent lower. The small plant case showed more variation but hydrogen addition still had the highest affordable price for crude with coking 25 percent lower. In this case, four

FIGURE 3.6

INVESTMENT COST VS. PITCH CONVERSION

(Arabian Light Crude)



undefined thermal processes had affordable prices for crude 2-25 percent below the hydrogen addition process.

These values suggest that there is some incentive to advance the development of the hydrogen addition processes. No standard economic values can be developed for these processes, however, because of wide variations in potential pitch feed properties, product qualities, product values and operating and capital cost factors. There are also important factors other than cost that will affect the process selection including:

- process risk and reliability
- simplicity and resulting ease of operability
- maintainability
- environmental acceptability
- projected oil and natural gas values
- other site specific factors.

The three major categories of conversion processes reviewed in the following sections are non-catalytic pyrolysis (Section 3.3.1), catalytic pyrolysis (Section 3.3.2) and hydrogen addition (Section 3.3.3). A review is given at the beginning of each main section of some of the fundamental work that has been done to understand the reaction mechanisms. This is followed by the reviews of the individual processes.

3.3.1 Non-Catalytic Pyrolysis

The general overall reaction that occurs during pyrolysis is:

Pitch → Gas Product + Liquid Product + Char.

The reaction is caused by a free radical chain reaction that is initiated by heating the hydrocarbon to high temperature. The process is complex since possible free radical reactions are numerous and the product spectrum can be large. In general, two types of reactions are important: degradation of the molecule to produce lighter components and polymerization/hydrogenation to produce coke. Established means of reducing the unwanted polymerization reactions include dilution and working at lower pressures.

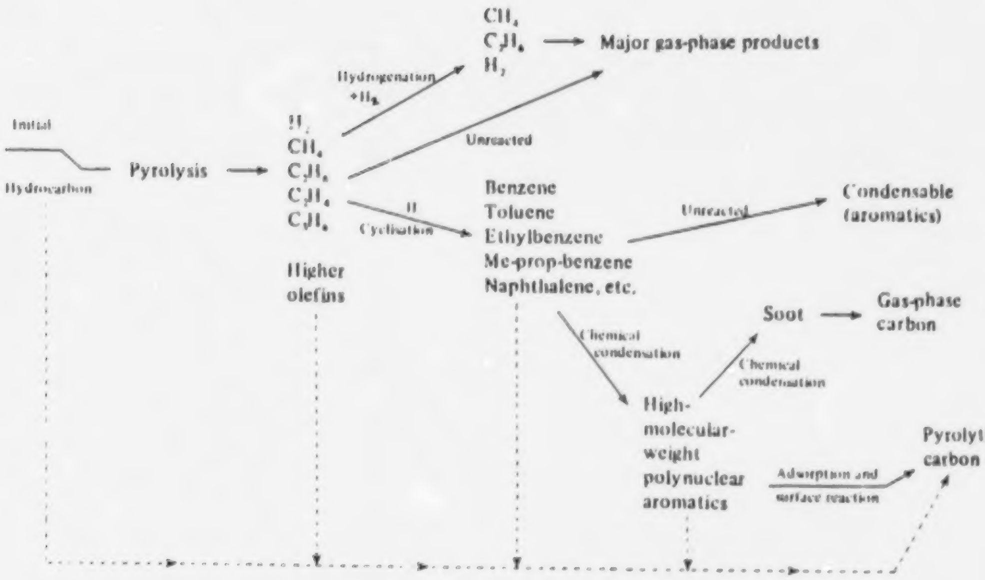
The important reactions are C-C bond breakage and free radical combination. Pyrolysis at low temperatures and high pressures favours C-C bond breakage near the centre of a hydrocarbon chain while high temperatures and low pressures favours bond breakage near the end of the chain resulting in more low molecular weight products. High temperatures and high pressures favour polymerization and coke formation along with production of low molecular weight products. The reaction sequence involves free radical initiation, propagation, branching and termination processes. A proposed overall reaction scheme is shown in Figure 3.7 (52). It has been found that there is an induction period for the production of tars and coke during which pyrolysis to produce lighter compounds can proceed. This is the basis for flash pyrolysis processes involving rapid heating and product quenching. The formation of coke is complex since it can be produced from reactions in the gas phase or on the surface of the reactor or the ash. The coke forming reactions and intermediates are still uncertain but it is felt that alkylaromatic molecules form coke easily and that polycyclic aromatic compounds may condense to form coke if their molecular weight is sufficiently large. Several processes have been developed involving pyrolysis in the presence of a diluent such as hydrogen or steam that reduce coke formation by reducing the probability of free radical combination (52). They also react chemically to stop the free radical chain reaction and can gasify coke under appropriate conditions.

Moschopedis et al (57) studied the thermal decomposition of asphaltenes separated from Athabasca bitumen. By evaluating the gas products formed, they concluded that at temperatures below 350°C the more thermally labile groups, such as those on peripheral sites, were eliminated while at temperatures above 350°C more severe degradation of the asphaltene molecule occurred. Thermal condensation reactions were found to occur as low as 250°C.

Ekwenchi et al (58) have studied pyrolysis of asphaltenes from several bitumen sources. From previous work, they note that the sulphur present in asphaltene may be mostly present as sulphide linkages which are pyrolysed at low temperatures,

FIGURE 3.7

PROPOSED PYROLYSIS REACTION SCHEME


Initial
Hydrocarbon
Pyrolysis
H_2
CH_4
C_2H_6
C_2H_4
C_3H_6
Higher olefins
Hydrogenation
$+H_2$
CH_4
C_2H_6
H_2
Major gas-phase products
Unreacted
H
Cyclisation
Benzene
Toluene
Ethylbenzene
Me-prop-benzene
Naphthalene, etc.
Unreacted
Condensable (aromatics)
Chemical condensation
High-molecular-weight polynuclear aromatics
Chemical condensation
Soot
Gas-phase carbon
Adsorption and surface reaction
Pyrolytic carbon

along with other reactive groups, and attacked by free radicals yielding low molecular weight polar compounds. Other work referenced found that asphaltene decomposition below 400°C was due to reaction of the least stable groups while above 400°C cracking of C-C linkages began to take place. Their results from high temperature (700°C) pyrolysis of asphaltenes showed first order kinetics of C_1-C_5 evolution with high alkene yield. This reaction is explained as primary cleavage of alkyl chains from the asphaltene followed by rearrangement, decomposition, hydrogen abstraction and combination - disproportionation reactions. The C_{11} - C_{22} hydrocarbon products analysis suggested their formation was a result of thermal decomposition of alkyl radicals. Low activation energies for Athabasca bitumen asphaltene decomposition led them to conclude that trace elements of mineral matter in the asphaltenes and the free radicals produced from decomposition of the less stable asphaltene fractions catalyze the further decomposition at high temperature.

Ritchie et al (59) have also measured pyrolysis of Athabasca tar sands asphaltene. The rate of reaction peaked at about 450°C and was nearly complete by 600°C. The coke produced at 800°C was not significantly different from that produced at 500°C but the gas:liquid product ratio was much higher. This indicates that liquid products produced at 500°C are converted by secondary decomposition to gaseous products at the higher temperature.

Furimsky (60) pyrolyzed both virgin and thermally hydrocracked pitches derived from Athabasca bitumen at up to 800°C. The maximum reaction rate occurred at about 500°C with the maximum for virgin pitch about 20°C below that for hydrocracked pitch. In spite of significantly different light product and char yields from the virgin and hydrocracked pitches, the char properties were similar for both feeds. This, and Ritchie et al's results above (59), suggest that residues from pyrolysis of organic materials approach the most stable, graphite-like structures when heated to elevated temperatures. The yield of volatile products from the thermally hydrocracked pitch was much lower than from the virgin pitch. It was suggested that this was a result of the removal of potential sites for cracking reactions during the thermal hydrocracking.

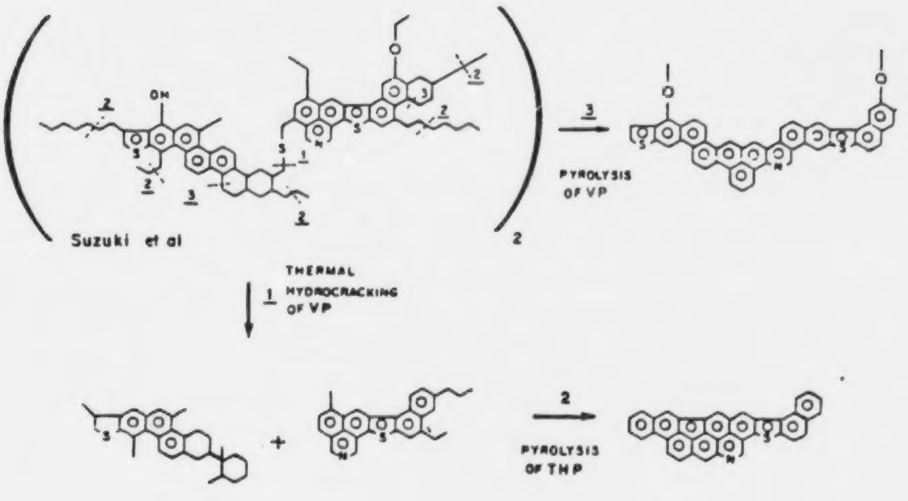
The general mechanisms suggested by Furimsky for the two types of pitch reactions are shown in Figure 3.8 (60). For simplicity, the volatile products are not shown in the mechanism. The bonds most susceptible to thermal cleavage are labelled by numbers. The C_{ali}-S bonds (1) are low strength and should be first to cleave. Extensive cracking will then occur at aliphatic chains attached to rings (2) resulting in formation of volatile products. Naphthenic rings (3), though more stable than aliphatic chains represent potential cracking sites. In this case dehydrogenation of the rings will compete with cracking but under thermal hydrocracking conditions the dehydrogenation will be suppressed.

Route 3 in the mechanism shows changes during pyrolysis of virgin pitch. Initial cracking reactions follow similar patterns to those during thermal hydrocracking but the absence of hydrogen results in combination of large radicals to high molecular weight species. Dehydrogenation of naphthenic rings further decreases the potential sites for cracking to volatile products to take place.

Route 1 is the mechanism proposed for thermal hydrocracking with only the heavy pitch molecules shown. Smaller molecules result because the hydrogen stabilizes the free radicals formed during cracking of C-C bonds. The amount of volatile products which can be produced by subsequent pyrolysis (Route 2) depends on the extent of reactions occurring in Route 1 and the remaining amounts of aliphatic chains, naphthenic rings and methylene bridges. The higher temperature required for the maximum rate with hydrocracked pitch suggests that the more reactive longer chains were removed during hydrocracking and that the pyrolysis reactions are methyl group cleavage as well as dehydrogenation and decomposition of naphthenic rings which explains the higher methane and hydrogen product yields than with the virgin pitch.

FIGURE 3.8

APPROXIMATE MECHANISM FOR THERMAL HYDROCRACKING AND PYROLYSIS


2
OH
S
1
3
2
Suzuki et al
2
3
PYROLYSIS OF VP
N
1
THERMAL HYDROCRACKING OF VP
+
2
PYROLYSIS OF THP

Sekhar and Ternan (61, 62) also measured pyrolysis of pitch from thermally hydrocracked Athabasca bitumen over a 350 - 1000°C temperature range. Up to 35 wt% of the original sample decomposed into volatile liquid and gaseous products with most of the reaction occurring between 400-500°C. The liquid products were higher in hydrogen and lower in aromatic content than the thermally hydrocracked pitch feed. The reaction had a 2 stage mechanism with 20% of the pitch decomposing by first order kinetics and the reaction then becoming more complex with the activation energy increasing with the extent of reaction. The kinetics of the latter stage are not well understood.

Two stage pyrolysis of conventional oil pitches and tar sand bitumens have been reported (63, 64). The first stage produces cracked oil products by heating the pitch feed at 440°C. This corresponds to the maximum reaction rate temperatures reported by researchers above. The cracked oils are then heated further to 700-800°C for less than 1 second to undergo further pyrolysis with the desired products being light olefins and aromatics. The two stage process with conventional oil pitches had ethylene yields equal to or better than yields from single stage pyrolysis processes discussed in the paper. The ethylene yields from pyrolysis of Athabasca bitumen at about 12 mass percent were only half those achieved with Taching crude pitch. This is attributed to the tar sand bitumen having shorter paraffinic straight chains and more branched molecules than the petroleum vacuum residues. A correlation was developed for the different feeds between ethylene yield and the fraction of straight chain paraffin carbons in the feed.

Pyrolysis of tars and volatile matter from coal carbonization was studied by Hesp and Waters (65) over a 400-1000°C temperature range. As the temperature increased there was more product gas and carbon formed and less residual tar. They deduced that the changes occurring at 500-700°C were mainly mild cracking of high molecular weight hydrocarbons, the removal of side chains from alkyl-aromatic compounds and aromatization of paraffinic and naphthenic compounds. At 600-700°C, the decomposition of tar acids started. The decomposition of aromatic rings started between 600° and 800°C depending on the reactor residence time. Above 900°C the cracking of low molecular weight paraffin hydrocarbons and residual aromatic compounds into carbon and hydrogen predominated along with the reactions of hydrocarbons and primary carbon with pyrolytic water.

Pyrolysis of a coal liquefaction oil was reported by Krishnamurthy et al (66) at temperatures of 600-750°C. They found preferential cracking of the saturates over the aromatics at all temperatures and residence times with the main gas products hydrogen, methane and ethylene. Polycyclic aromatics formed in the liquid product. The rate of cracking was found to follow first order kinetics.

The preceding review of pyrolysis research and proposed mechanisms, illustrates that a wide variety of feeds and process conditions have been studied and that the detailed chemistry involved is open to doubt. This reflects the complex mixture of organic compounds present in the pitch and the multitude of free radical reactions which are possible. As a result, the operation of many of the processes to produce carbon or usable light hydrocarbons are often based primarily on experience. The research shows that the maximum cracking rate and conversion to lighter liquid products will occur at 400-500°C. Reactions at higher temperatures, up to 1000°C, will convert the primary cracking products to light gas products.

Some of the commercially practised processes based on non-catalytic pyrolysis are reviewed below with a brief process description, typical yield and product quality data, and economic parameters when available. The overall reaction mechanism has been presented above and is not discussed with each process.

(a) Visbreaking

Visbreaking is the mildest of the pyrolytic thermal cracking processes. Its main purpose has been to lower the viscosity and pour point of the residual oil feed thus reducing the amount of cutter stock required for blending to meet the fuel oil viscosity specification as discussed in Section 3.2.1. UOP has reported (12) the commercial operation of a visbreaker on pitch from a solvent deasphalting unit that resulted in a 40% reduction of required cutter stock and a 20% reduction in heavy fuel oil product. The process variables which have most effect on visbreaking operations are furnace residence time, visbreaking temperature, feedstock characteristics, soaking section residence time and furnace operating pressure. The key parameters are residence time and temperature. There are two main process types shown in Figure 3.9 (23) which reflect different views of the time-temperature relationship.

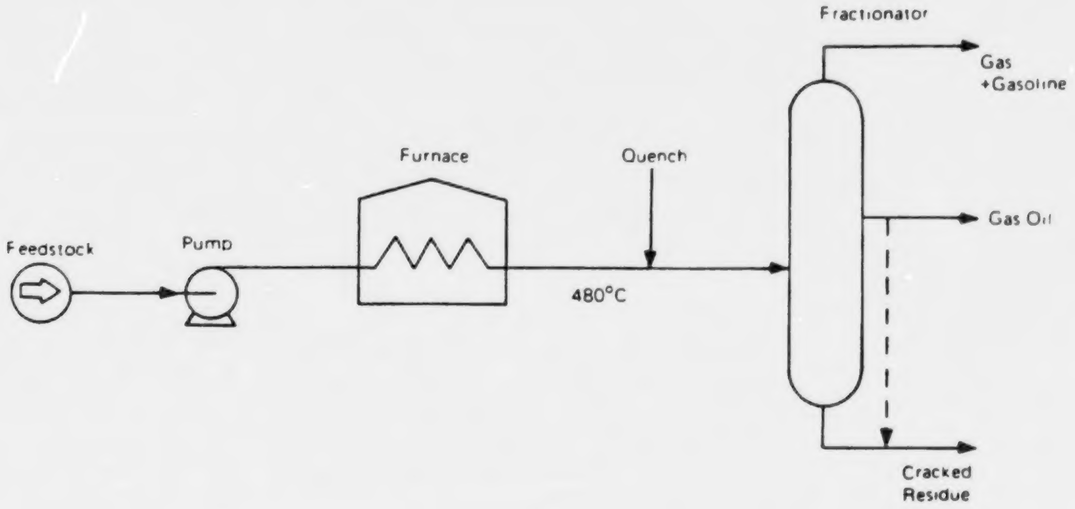
(i) The coil type uses a higher temperature and shorter reaction time. It consists of a furnace where the visbreaking reaction takes place and a fractionator which separates the products after quenching to stop the cracking reactions. The process typically operates at furnace outlet conditions of 470-490°C and 1.5 - 1.8 MPa. The coil design is offered by a number of licensors including M.W. Kellogg, Technip and Exxon.

(ii) The soaker type operates at a lower temperature and has a soaking drum to give additional residence time for the cracking reactions before quenching. The process operates at 450-460°C furnace outlet temperature and 430-435°C soaking drum outlet temperature at 0.6 - 1.6 MPa. Eight minutes residence time at 440°C will give the same yield of 165°C and lighter products as one minute at 485°C (67). The main advantages claimed for the less severe soaker operation are a smaller furnace, lower fuel consumption, more selective yield, longer furnace run lengths and better process control. The soaker process is a Shell design licensed by Lummus-Crest.

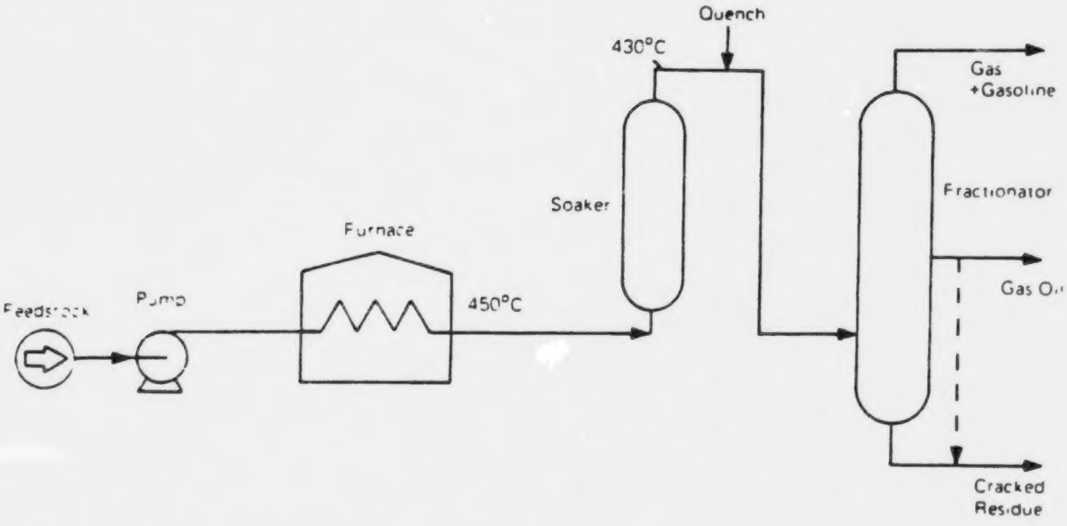
The amount of cracking that occurs during the process is usually expressed in terms of the yield of product material lighter than 350°C and is referred to as the conversion. Conversions of 15-20 mass percent can be typically achieved from a 525°C+ pitch feed. The maximum conversion is limited by the

FIGURE 3.9

VISBREAKER PROCESS FLOW SCHEMATIC


Fractionator
Gas
+Gasoline
Furnace
Quench
Gas Oil
Feedstock
Pump
480°C
Cracked
Residue

Coil Type


Quench
430°C
Gas
+Gasoline
Fractionator
Soaker
Furnace
Gas Oil
Feedstock
Pump
450°C
Cracked
Residue

Soaker Type

product tar quality or furnace coil coking. The product tar quality parameters of concern are asphaltene content, sediment content and/or incompatibility. Incompatibility refers to the susceptibility of the asphaltenes in the visbreaker pitch to form sediment during fuel oil blending or storage.

It is theorized that asphaltenes exist in residua as the centre of a colloidal particle or micelle with the central part consisting of the asphaltene covered by a high molecular weight, highly branched aromatic structure which is surrounded by constituents of a lower degree of aromaticity. These aromatic structures, maltenes, hold the micelle in physical equilibrium with the surrounding oil phase in a stable system. During visbreaking, the continuous oil phase is cracked to smaller molecules, new asphaltenes are formed from maltenes and the maltene phase changes composition so that eventually the equilibrium between asphaltenes and maltenes is disturbed to the point the asphaltenes flocculate. This is the point that limits the cracking conversion. Several authors have discussed this in more detail (67- 69).

This conversion limit of 15-20 percent and the resulting high yield of low quality visbreaker pitch has limited the use of visbreaking with pitches containing a high level of impurities. Some yield correlations have been published (70, 71) and some typical yields and product qualities are shown in Table 3.2. The high yield and sulphur content of the visbroken pitch from the Athabasca bitumen makes the process unattractive for that application.

Economics for the coil and soaker processes show the soaker design to be less expensive (4, 23) as shown in Table 3.3. Lummus (4) gives a 1984 battery limits cost of a 3975 m^3/d visbreaker in N.W. Europe of $21 million U.S. including fractionation and gas recovery but excluding treating facilities. The claimed advantages for the soaker design have been disputed by some authors (74, 75). Wood (75) shows that the coil cracker costs can be lower when downstream fractionation and cutter stock requirements are included in the evaluation.

TABLE 3.2

VISBREAKING YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Bromine Number	Conradson Carbon Mass Percent
(i) Light Arabian Vacuum Pitch (72)						
Feed	100.0	6.9	4.0	3100		
Products						
C_4-	2.5					
C_5/C_6	1.3	82.0	0.8			
C_7-185°C	4.6	51.0	1.0	50	62	
185-343°C	8.8	32.5	1.6	1000	28	
343-565°C	19.4	16.5	3.1	2000	8	
565°C+	63.4	0.8	4.6			
(ii) Whole Athabasca Bitumen (73)						
C_4-	3					
C_5-221°C	7	54	2.0	110	115	
221-343°C	21	25.8	2.1	450	38	
343-538°C	35	13.2	3.9	2800	20	0.23
538°C+	34					

TABLE 3.3

VISBREAKER ECONOMICS

	Coil	Soaker
(i) Utility Requirements per m^3 Fresh Feed		
Electricity, kWh	3.0	4.0
Cooling water, m^3	6.4	4.0
Fuel, MJ	580	410
Steam produced, kg	(24)	(17)
(ii) Capital Cost	Base	0.85-0.90 Base

( ) Amount produced

(b) Delayed Coking

Delayed coking is a well proven technology in which the residuum is rapidly heated in a furnace and confined in a coke drum reaction zone where vapour products and coke form as a result of the pyrolysis reactions discussed earlier. An additional coke forming mechanism that is important with higher Conradson carbon content feedstocks is related to asphaltene flocculation as discussed with visbreaking. In coking, the colloidal suspension of asphaltene and resin compounds is distorted by the thermal cracking resulting in the precipitation of compounds to form a highly cross linked structure of amorphous coke. There is also significant cleavage of aliphatic groups increasing the C/H ratio of the coke.

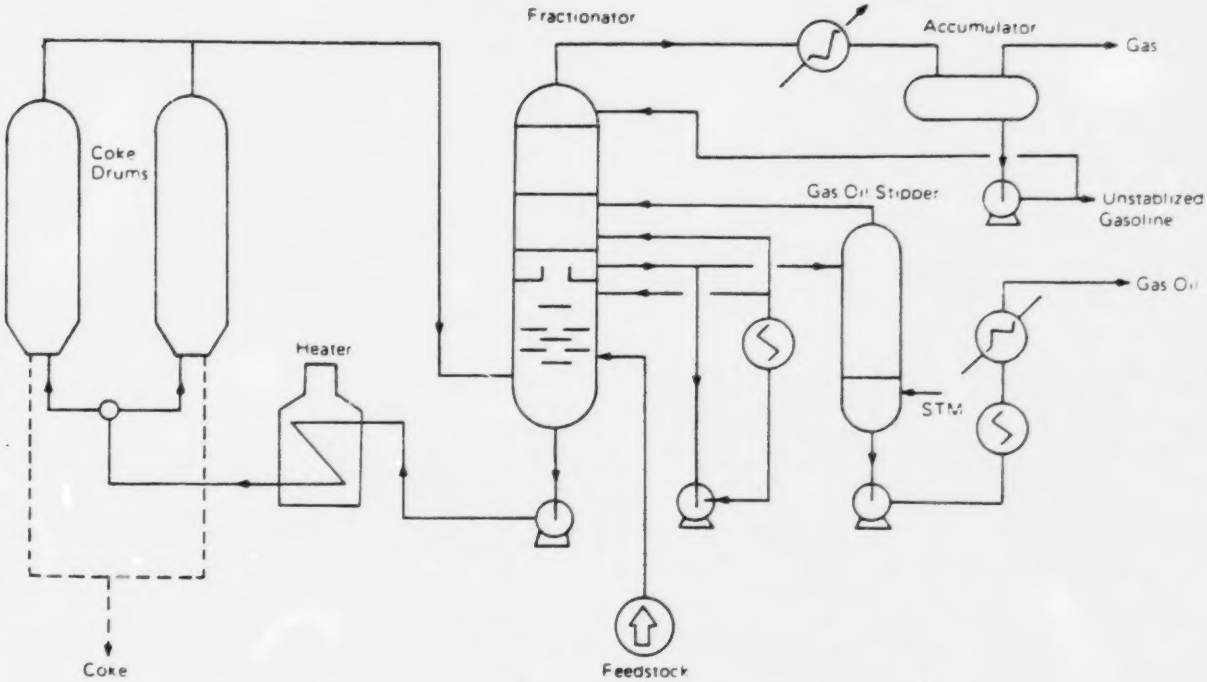
The coke has high impurity levels since it is formed from asphaltenes and with its amorphous nature it is undesirable for high grade carbon anodes. The coke formed by the polymerization and condensation reactions discussed previously has fewer crosslinkages and is more crystalline than the precipitated asphaltene coke. When formed from an aromatic feed, this latter coke is a premium grade electrode coke (76). The formation of these two coke types during thermal hydrocracking is also discussed by Belinko and Denis (77).

A typical process flowsheet is in Figure 3.10 (23). Fresh feed and unreacted recycle pitches are heated to 480-510°C furnace outlet temperature before entering the coke drums. The drums operate on a batch basis and alternate between the coke reaction phase and product coke removal. The product vapours from the drum at 430-450°C and 0.2 - 0.8 MPa flow to the fractionator where they are quenched and cracked distillate products are recovered.

The key operating variables are temperature, pressure and recycle ratio. Temperature is used to control the volatile content of the coke in the 8-10 mass percent range. Higher temperatures increase the reaction rate and decrease the coke yield but if the temperature is too high the volatile content will be reduced producing hard coke that is difficult to remove from the drums. An increase in coke drum pressure causes more of the heavier hydrocarbons to be retained in the drum until they crack resulting in an increase of coke and gas yield at the expense of distillate product yield. An increase

FIGURE 3.10

DELAYED COKING PROCESS FLOW SCHEMATIC


Fractionator
Accumulator
Gas
Coke Drums
Gas Oil Stripper
Unstablized Gasoline
Gas Oil
Heater
STM
Coke
Feedstock

in recycle ratio from the fractionator has the same effect and is an interchangeable variable with pressure. Recycle is used primarily to control the end point of the coker gas oil (78, 79).

Delayed coking yield correlations have been published (80, 81) and two typical yields are in Table 3.4. The sulphur content of the delayed coke from Athabasca bitumen has been reported as 4.6 - 5.3 mass percent (82). The coke yield depends on the Conradson carbon content of the feed and the operating conditions. It would be determined by pilot plant testing but very roughly the coke yield is 1.5 - 2 times the Conradson carbon content and the sulphur in the coke is 1.2 - 1.5 times the concentration in the feed. The conversion of pitch to distillable products is usually in the 60 - 75 percent range. All of the ash and metal impurities in the feed will concentrate in the coke. With many of the heavier pitch feeds this can result in a coke product that can only be used for fuel with sulphur capture from the flue gas.

The major potential uses for coke are as non-graphitized electrodes for aluminum manufacture, and for carbon and graphite manufacture. Typical specifications for these two uses are in Table 3.5 which show that only cokes from reasonable quality pitches will have uses other than fuel.

Needle coke is a specialized crystalline coke preferred for graphitized electrodes. It is produced from highly aromatic pitches such as catalytic cracking decant oil and pyrolysis tar from olefin cracking (85).

Utility consumption data for a 1590 m^3/d delayed coking plant are (23):

Fuel	84 GJ/h
Power	600 kW
Steam	13 t/h
Cooling Water	2000 t/h

A current capital cost was not available but will be more than a similar capacity visbreaker.

The process is licensed by Foster Wheeler, M.W. Kellogg, Lummus-Crest, Conoco, UOP and others.

TABLE 3.4

DELAYED COKING YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	Ni+V mg/kg	Conradson Carbon Mass Percent
(i) Light Arabian 565°C+ Pitch (78)					
Feed	100.0	7.4	4.1		15.4
Products					
C_4-	11.1				
C_5-193°C	16.1	58.8	1.0		
193°C+	45.8	28.1	2.3		
Coke	27.0		6.4	366	
(ii) Whole Athabasca Bitumen (73)					
C_4-	7.9				
C_5-204°C	12.7	46.8	2.2		
204-277°C	15.0	32.9	2.7		
277-454°C	42.2	18.3	3.8		
Coke	22.2				

TABLE 3.5

PETROLEUM COKE SPECIFICATIONS

(i) Typical aluminum anode coke specifications (83)	Green	Calcined
Volatiles, mass percent (maximum)	12	0.5-0.6
Metals, mg/kg (maximum)		
Silicon	200-300	200-300
Iron	300	300
Vanadium	200-250	200-250
Other metals	300	
Sulphur, mass percent (maximum)	2.5-4.0	2.5-3.0
Bulk density, g/cm^3 (mimimum)	-	0.8

(ii) Typical properties of petroleum coke used in carbon and graphite manufacture (84)	Green Coke	Coke Calcined to 1300°C
Aluminum, mg/kg	15-100	15-100
Boron, mg/kg	0.1-0.5	0.2-1.5
Calcium, mg/kg	25-500	25-500
Fixed carbon, percent	87-97	97-99
Hydrogen, percent	3.0-4.5	0.1
Iron, mg/kg	50-2000	50-2000
Manganese, mg/kg	2.0-100	2.0-100
Magnesium, mg/kg	10-250	10-250
Nickel, mg/kg	10-100	10-100
Nitrogen, percent	0.1-0.5	0.1
Silicon, mg/kg	50-300	50-300
Sulphur percent	0.2-2.5	0.2-2.5
Titanium, mg/kg	2.0-60	2.0-60
Vanadium, mg/kg	5.0-500	5.0-500
Moisture, percent	0.5-2.0	Negligible
Volatile matter, percent	5.0-15	0.2
Real density, g/cm^3	1.6-1.8	2.08-2.13
Ash, percent	0.1-1.0	0.2-1.5

A variation of the process operating under a hydrogen partial pressure, to improve the product yields and qualities, is in the early development stages in Germany (86).

(c) Eureka

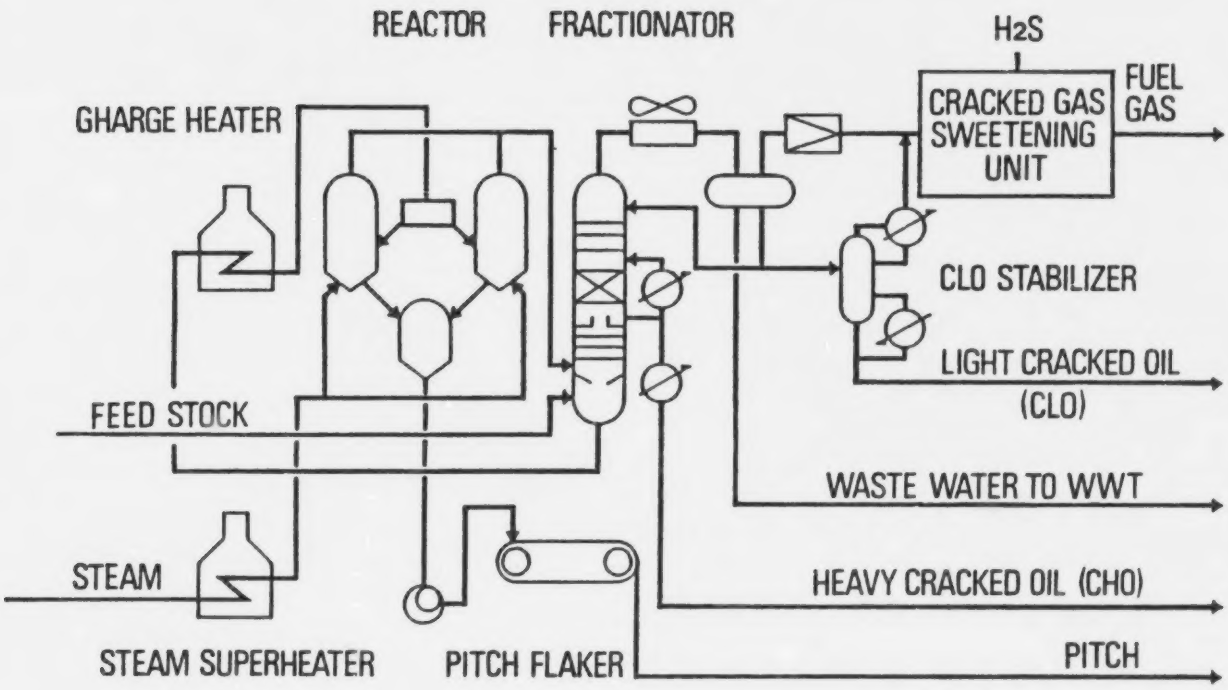
The overall concept of the Eureka process is similar to delayed coking except that a liquid pitch residue is produced rather than a solid coke. A schematic flowsheet of the process is in Figure 3.11 (28). The feed and recycle pitches from the fractionator are heated to about 500°C and fed to one of the two reactor drums. The reaction in the drum occurs at 415-430°C and 0.13 - 0.14 MPa for about 2 h. These temperature, pressure and time conditions are all lower than with delayed coking. The reactor turnaround time of about 4 hours compares to 24 hours with delayed coking and results in much smaller reactor drums for a given throughput. As with delayed coking, there is not a lot of flexibility with the reaction time. If it is left too long the condensation reactions will proceed too far and the pitch will solidify. If the reaction time is too short, the pitch yield will be too high and it will have a low softening point. At the end of the reaction, the pitch is quenched to 350°C and pumped from the drum where it can be stored as a liquid or flaked to a solid.

The product vapours from the reactor drum flow to the fractionator. Because of the effect the steam has on hydrocarbon partial pressure, the cracked light oil flows as a vapour from the top of the fractionator and is then produced from the cracked light oil stabilizer.

The unique part of the process is that the reacting pitch is continuously blown with superheated steam at about 700°C during the reaction. The discussion of the pyrolysis reaction mechanisms at the beginning of Section 3.3.1 noted that an established means of reducing unwanted polymerization was by dilution, such as steam, and working at lower pressures. The effect is to vapourize more primary cracked products from the reactor to be recovered as distillate products. This prevents secondary cracking to gas products and subsequent condensation reactions to form additional pitch and ultimately coke. This primary product vapourization also allows operation at a lower reactor temperature which reduces the light gas product yield. The overall result is a higher distillate product yield and lower yields of gases and pitch residue than with delayed

FIGURE 3.11

EUREKA PROCESS FLOW SCHEMATIC


REACTOR
FRACTIONATOR
H2S
GHARGE HEATER
CRACKED GAS SWEETENING UNIT
FUEL GAS
CLO STABILIZER
LIGHT CRACKED OIL (CLO)
FEED STOCK
WASTE WATER TO WWT
STEAM
HEAVY CRACKED OIL (CHO)
PITCH
STEAM SUPERHEATER
PITCH FLAKER

coking (coke residue) (28, 87-89). Figure 3.12 shows a comparison of the Eureka and delayed coker pitch/coke yields which confirms this conclusion (89). The pitch yield is about 1.45 times the Conradson carbon content of the feed (4) compared to 1.5 to 2.0 times with delayed coking. Typical yields and product properties are in Table 3.6 (28, 87). More detailed pitch properties are in Section 4.0.

Utility requirements for a 3180 m^3/d Eureka process plant are (87):

Steam @ 300°C, 1.6 MPa	16,800 kg/h
Electricity	2,850 kW
Fuel	239 GJ/h
Boiler feed water	49 m^3/h
Cooling water (10°C ΔT)	2,500 m^3/h

Up-to-date capital cost data have not been published but an overall processing cost of 1.1¢ U.S./kg of feed charged has been given (4).

A 3180 m^3/d plant has operated since 1976 in Japan and a second 3180 m^3/d plant has been reported for several years as under construction in China. The pitch from the Japanese plant has been used as a binder for coke in steel production and as pulverized boiler fuel.

The process is licensed by Kureha Chemical Industry Co. with Chiyoda Chemical Engineering & Construction Co.

(d) Fluid Coking

The Fluid Coking process, licensed by Exxon Research and Engineering since the mid-1950's, is significantly different from the two previous processes since it is continuous and operates at higher severity. The continuous operation is maintained by operating with a circulating bed of fluidized coke particles that act as heat carrier, site for coke production, and means of removing product coke continuously from the reactor. The general concept is similar to a fluid catalytic cracking unit with the coke particles replacing the catalyst.

FIGURE 3.12

PROCESS RESIDUE YIELD VS. FEED CONRADSON CARBON

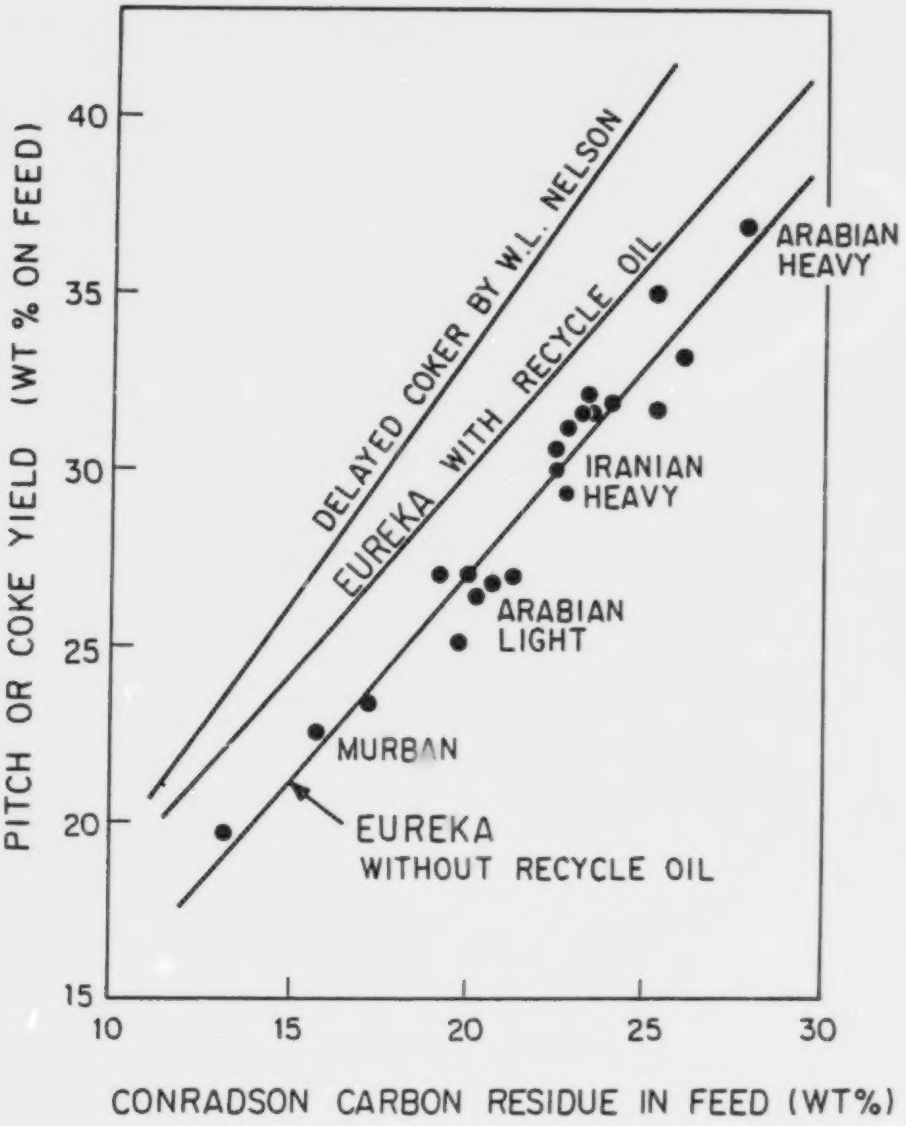


TABLE 3.6

EUREKA PROCESS YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Bromine Number	Softening Point, °C
(i) Light Arabian 538°C+ Pitch (87)						
Feed	100.0	8.0	4.2			
Products						
C_4-	5.2					
C_5-238°C	11.3	51.8	1.5		89	
238-538°C	53.4	21.5	2.7		35	
538°C+	30.1		6.9			182
(ii) Whole Athabasca Bitumen (28)						
Feed	100.0	9.0	4.3	3700		
Products						
C_4-	3.6					
C_5-190°C	7.5	56.9	1.7	< 100	73	
190-315°C	18.2	29.1	2.2	200	30	
315-525°C	52.0	14.5	3.1	3000	22	
525°C+	18.7		6.6			200
(iii) Athabasca Bitumen 500°C+ Pitch (28)						
Feed	100.0	2.0	5.7	5600		
Products						
C_4-	4.6					
C_5-190°C	7.5	62.6	1.9	< 100	77	
190-315°C	13.1	31.9	3.5	400	52	
315-525°C	42.8	14.4	3.9	2500	26	
525°C+	32.0		6.6			200

A process flow diagram is in Figure 3.13 (23). The feed and recycle pitches at 250-400°C are sprayed into the fluidized bed of coke particles in the reactor. The reactor operates at higher severity than any of the above processes: 510-560°C, 0.14-0.18 MPa, 15-20 seconds residence time (52, 90, 91). Part of the feed is vapourized immediately and flows into the scrubber. The remainder is deposited on the coke where cracking and polymerization reactions occur. Because of the high temperature, the cracking occurs rapidly with the cracked products readily vapourized from the coke particles at the low operating pressure. The product vapours flow through a cyclone for removal of coke particles and are then quenched in the scrubber at about 380°C. The heavy components condensed at this temperature are recycled to the reactor while the product vapour flows to a fractionator for separation into distillate products and gas.

Most of the pyrolytic coke and inorganic feed material deposit on the coke particles in the reactor. As particles become heavier they sink to the bottom of the reactor where steam stripping removes entrained hydrocarbons and the coke flows to the burner. The burner provides the heat for the cracking reactions by burning about 40% of the gross coke product in an air fluidized bed. The burner operates at 610-680°C with coke particles being continuously recycled to the reactor at this temperature. Since only partial combustion occurs, the flue gas contains CO which is usually burned in a CO boiler for energy recovery. The net product coke not burned for cracking heat is continuously removed from the burner through a quench system.

In Section 3.3.1 it was stated that pyrolysis at high temperature and low pressure favours bond breakage near the end of the chain. This results in the formation of more lighter products. The operating conditions also result in a low cracked product residence time which reduces condensation reactions and, therefore, coke yield. This is illustrated by the yields shown in Table 3.7 (92). The coke yield has been found equal to 0.8 to 1.2 times the Conradson carbon content with the lower value applying for reduced heavy oil recycle to the reactor (90). The cracked products are lower in quality than from the less severe processes, having more olefinic constituents.

FIGURE 3.13

FLUID COKING PROCESS FLOW SCHEMATIC

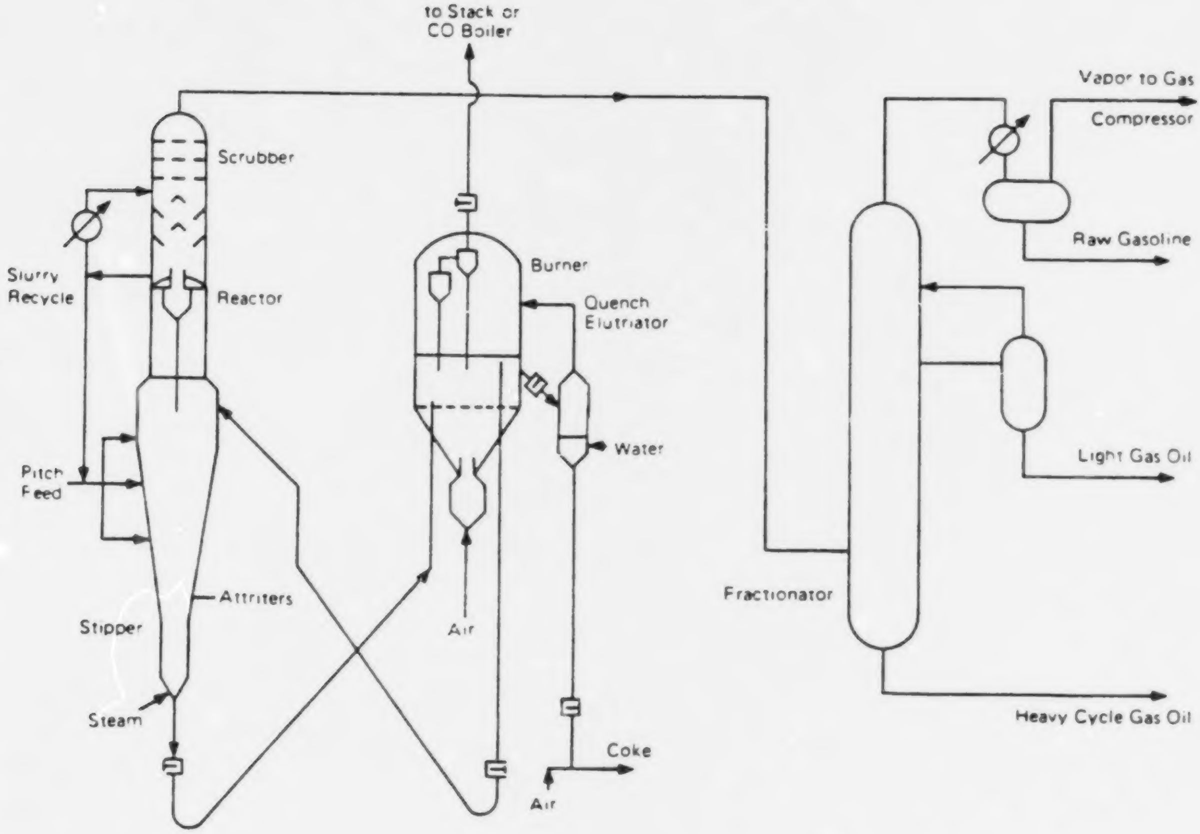

to Stack or
CO Boiler
Vapor to Gas
Compressor
Scrubber
Slurry
Recycle
Reactor
Burner
Quench
Elutriator
Raw Gasoline
Water
Light Gas Oil
Pitch
Feed
Attriters
Stipper
Fractionator
Air
Steam
Heavy Cycle Gas Oil
Coke
Air

TABLE 3.7

FLUID COKING YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Conradson Carbon Mass Percent
(i) Heavy Arabian Vacuum Residuum (92)					
Feed	100.0	3.0	6.0	4800	27.7
Products					
C_4-	13.8				
C_5-177°C	10.3	58.2	1.1	70	
177-343°C	15.1	28.7	3.4	950	0.14
343-510°C	25.0	10.3	5.8	4600	4.8
Gross Coke	35.8		7.0		
(ii) Whole Athabasca Bitumen (92)					
Feed	100.0	8.9	4.9	4000	12.7
Products					
C_4-	8.7				
C_5-221°C	13.8	50.8	2.2	60	
221-343°C	21.2	23.7	3.2	800	0.03
343-510°C	41.1	12.4	4.5	2600	1.8
Gross Coke	15.2		6.8		

Economics for processing Arabian Heavy pitch (565°C+) are given in Table 3.8 (23).

(e) Flexicoking

The Flexicoking process is a development of Fluid Coking and is also licensed by Exxon Research and Engineering. The reactor part of the process, the hydrocarbon product yields and their properties are all the same as with Fluid Coking and will not be repeated in this Section. The main process difference is that the net coke product is gasified within the process to a low heating value fuel gas. Only a small purge coke stream is now produced and about 98 percent of the pitch feed is converted to gaseous and liquid products.

A schematic flow diagram is in Figure 3.14 (93). The coke formed in the reactor is withdrawn by a circulating coke stream and passed into the heater vessel. In the heater vessel, the coke is pyrolyzed at about 620°C to yield methane and residual coke. Some of the hot coke is recirculated to the reactor to provide the heat for cracking reactions. The remainder is circulated to the gasifier vessel where it is reacted with air and steam at 815-980°C to form a mixture of hydrogen, water, carbon monoxide, carbon dioxide, nitrogen, hydrogen sulphide and trace amounts of carbonyl sulphide. The coke inventory is controlled by the gasifier air rate and the temperature by the steam rate. The coke gas flows through the heater where it provides heat for pyrolysis in the reactor. The gas from the heater is cooled and cleaned of solids and sulphur producing a low heating value fuel gas of about 3.7-4.5 MJ/Nm^3. The product purge coke yield is only about 2 mass percent on feed as required to remove inorganic components from the process and contains only 2 mass percent sulphur. About 95 percent of the sulphur in the pitch feed can be recovered from the fuel products as elemental sulphur. The gas normally contains about 50 volume percent nitrogen with heavy pitch feeds. Commercial units have operated in Japan and Venezuela (23, 92-94).

A new version of the process being developed by Exxon is to separate the air and steam gasification reactions in separate vessels for applications where the low heating value fuel gas cannot all be used within the plant. Dual Gasification Flexicoking reduces the coke gas production and produces a hydrogen rich synthesis gas. Schematics of the flowsheet and the reaction mechanisms are in Figure 3.15 (93). The reactor

TABLE 3.8

FLUID COKING ECONOMICS

(i) Capital cost

Plant Capacity, m^3/d	4770
Total Prime Contract Cost, 10^6 US$ (1974) Including CO boiler and electrostatic precipitator but excluding flue gas desulphurization	26

(ii) Utilities Consumption

Power	7890 kW
Steam, high pressure, produced	112 t/h
Steam, low pressure, required	7.3 t/h
Boiler Feed Water	186 t/h
Cooling Water	501 t/h
Process Water	12.5 t/h

FIGURE 3.14

FLEXICOKING PROCESS FLOW SCHEMATIC

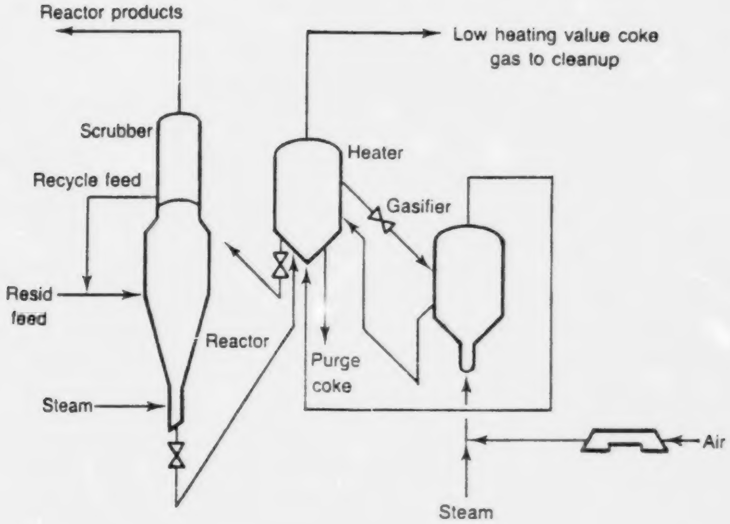
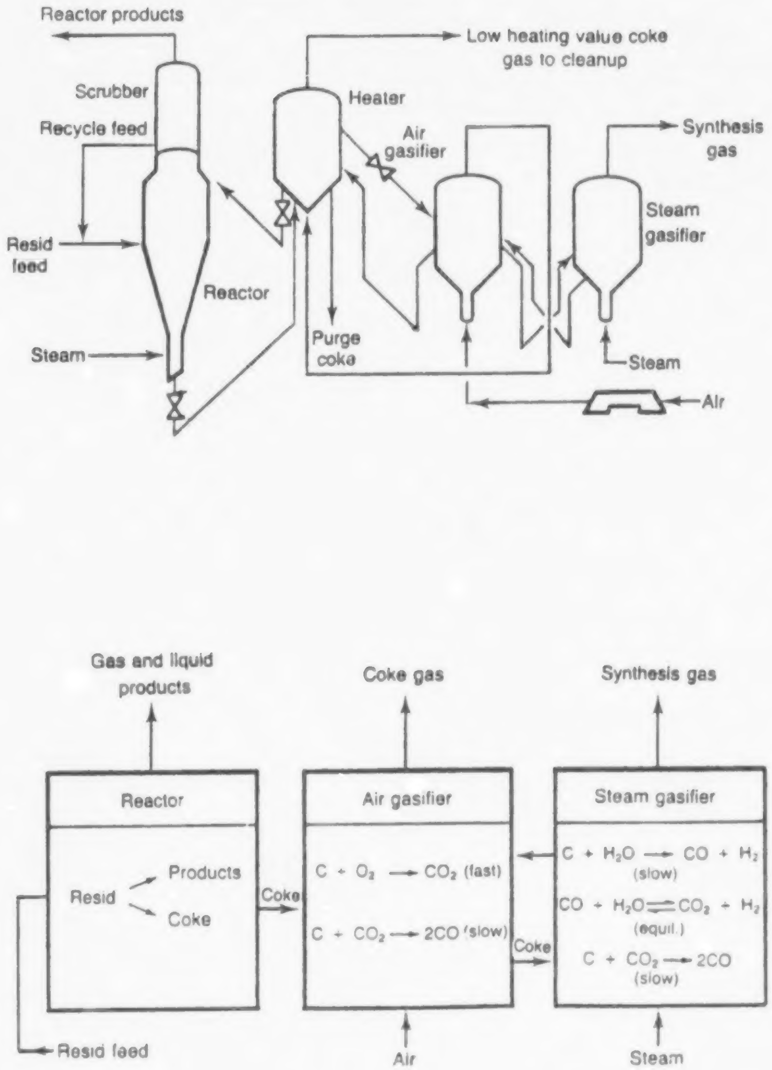

Reactor products
Low heating value coke gas to cleanup
Scrubber
Heater
Recycle feed
Gasifier
Resid feed
Reactor
Purge coke
Steam
Air
Steam

FIGURE 3.15

DUAL GASIFICATION FLEXICOKING PROCESS FLOW SCHEMATIC AND REACTION MECHANISMS


Reactor products
Scrubber
Recycle feed
Resid feed
Reactor
Steam
Low heating value coke gas to cleanup
Heater
Air gasifier
Purge coke
Synthesis gas
Steam gasifier
Steam
Air
Gas and liquid products
Coke gas
Synthesis gas
Reactor
Resid
Products
Coke
Coke
Air gasifier
C + O$_2$ → CO$_2$ (fast)
C + CO$_2$ → 2CO (slow)
Coke
Steam gasifier
C + H$_2$O → CO + H$_2$ (slow)
CO + H$_2$O ⇌ CO$_2$ + H$_2$ (equil.)
C + CO$_2$ → 2CO (slow)
Resid feed
Air
Steam

and heater function in the same way as in a conventional Flexicoking unit. In the air gasifier, coke is burned with air to provide reaction heat for both the reactor and the steam gasifier with resulting production of low heating value gas. In the steam gasifier a hydrogen/carbon monoxide rich synthesis gas free of nitrogen is produced which can be used in a variety of ways (see Section 3.4). The Dual Gasification Flexicoking process is very similar in overall concept to CANMET's pyrolysis/ gasification process, the main difference being that Flexicoking is non-catalytic.

The gas yields and compositions from the two Flexicoking process versions are in Table 3.9 showing the shift in fuel gas production for an Arabian Heavy vacuum pitch feed. The low heat content coke gas production rate is reduced by 21% and the contained heat duty in the gas by 46% in the dual gasifier option (93). The synthesis gas is equivalent to 0.35 Nm^3 hydrogen/m^3 pitch feed.

Exxon has done some economics comparing the total installed cost of the two Flexicoking process versions and found them almost equal with the fuel gas/synthesis gas price spread determining the better route (93). Published investment and utility values for the process are in Table 3.10 (4). As well as operation with petroleum pitches, the process has been evaluated for processing Exxon Donor Solvent coal gasification pitch (94).

(f) Lurgi-Ruhrgas

The Lurgi-Ruhrgas or L-R process was originally developed jointly by Lurgi and Ruhrgas beginning in 1949 for carbonizing coal and producing olefins from naphtha and crude oil. Development of the process has continued and it is now proposed for cracking bitumen in a whole mined oil sands feed or for cracking pitch to lighter products. It is this latter application that is relevant for this study. The basic concepts of the L-R process with pitch feed are the same as the Fluid Coking process described in Section 3.3.1 (d).

A schematic of the L-R process is in Figure 3.16 (96). As with Fluid Coking, the pitch feed is pyrolyzed with the reaction heat provided by a circulating bed of coke particles. Some of the coke is burned to heat the circulating coke returning to the reactor section. The double screw mixer

TABLE 3.9

FLEXICOKER PRODUCT GAS

	Conventional Flexicoker Coke Gas	Dual Gasification Flexicoker	
		Coke Gas	Synthesis Gas
Coke gasified, percent	97 By Air	69 By Air	28 By Steam
Gas rate, Nm^3/m^3 pitch	1.94	1.53	0.44
Composition, volume percent			
CO	19.4	11.7	26.0
CO_2	7.5	11.8	11.1
H_2	17.0	9.7	52.9
H_2O	12.7	10.1	8.5
N_2	41.3	54.3	-
Other	2.1	2.4	1.5
Heating value, MJ/Nm^3	4.8	3.2	9.2

TABLE 3.10

FLEXICOKER ECONOMICS

(i) Capital Cost

1983 U.S. Gulf Coast, $U.S. per m^3/d pitch capacity	6290-14,470

Basis: Battery limit onsite including fractionator but excluding coke gas sulphur removal.

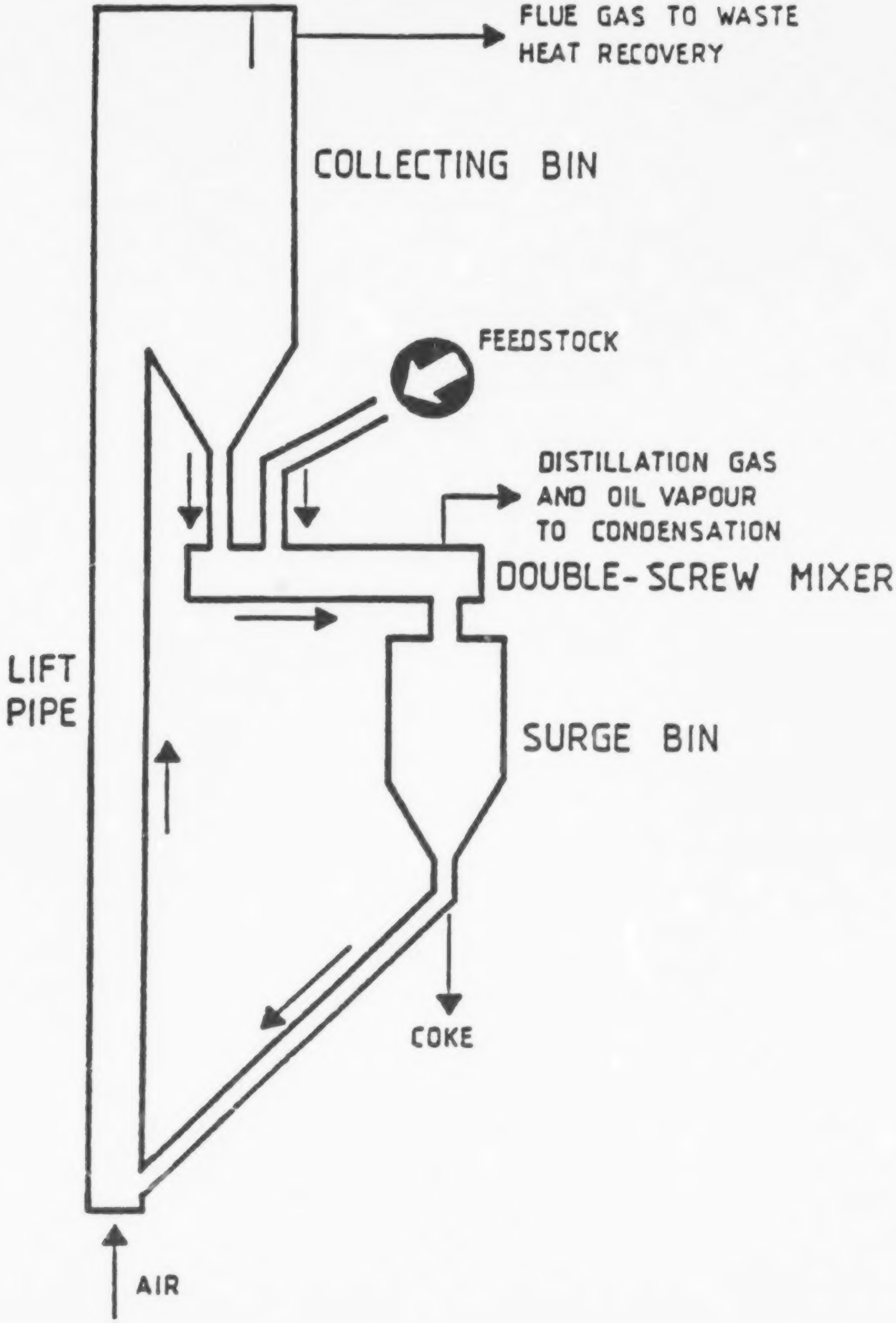
(ii) Utilities Consumption, per m^3 feed

Steam, 1 MPa	285 kg
Steam, 4.2 MPa	(570 kg)
Electricity	82 kWh
Cooling water	9.5 m^3
Boiler feed water	0.7 m^3

( ) Amount produced

FIGURE 3.16

LURGI-RUHRGAS PROCESS FLOW SCHEMATIC


FLUE GAS TO WASTE HEAT RECOVERY
COLLECTING BIN
FEEDSTOCK
DISTILLATION GAS AND OIL VAPOUR TO CONDENSATION
DOUBLE-SCREW MIXER
LIFT PIPE
SURGE BIN
COKE
AIR

blending the feed and heat carrier is the pyrolysis reactor and operates at 510-550°C for producing distillate fuel products from pitch feed. The coke heat carrier to feed weight ratio is about 5-8 which is the same range as with a fluid catalytic cracker and as would be expected with Fluid Coking. The pyrolysis vapour products are separated from the heat carrier and solid pyrolysis residue, are dedusted in cyclones, cooled and sent to a fractionator for recovery of the product streams. The volatile pyrolysis products have a residence time in the reactor of only a few seconds which should minimize some of the coke forming free radical reactions. The coke particles fall to a lift pipe where they are partially combusted by being lifted with air. The combustion air rate controls the pyrolysis temperature. In the collecting bin, the hot coke is separated from the flue gas which is routed to a CO boiler, heat recovery and purification. The hot coke at about 600°C is recycled to the pyrolysis reactor. The net coke product is continuously removed from the system via a cooling system for heat recovery. When used for retorting whole oil sand, the heat carrier is sand rather than coke particles (96).

Because of the very similar reaction conditions, the reaction mechanisms, product yields and qualities should be about the same as with Fluid Coking. Data from pyrolysis of Athabasca bitumen and the vacuum pitch from a Venezuelan heavy oil are in Table 3.11. Since the product distilling above 520°C has not been recycled back to the reactor, the yields cannot be directly compared to those shown in Table 3.7 for Fluid Coking. The high Bromine numbers show that these products are highly olefinic.

Economic data and utilities have not been published for this process. A thermal efficiency of 89% was given (94) for cracking whole Athabasca oil sand with the sand and flue gas rejected at 200°C.

Different versions of the process have been developed by others for the direct cracking of mined oil sands. Taciuk has been developing a kiln based process since 1974. The process has progressed through testing on a 91 t/h pilot plant and is ready to proceed to a larger scale commercial demonstration (95, 97, 98). Bench scale cracking of whole Athabasca oil sand was also done at Syncrude (99), where they concluded the yields were similar to whole bitumen pyrolysis yields but that

TABLE 3.11

LURGI-RUHRGAS YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Bromine Number	Conradson Carbon Mass Percent
(i) Whole Athabasca Bitumen (96)						
Feed	100.0		5.7	6000		15.6
Products						
Gas	11.0					
C_5-182°C	1.9	42.2	1.8	1000	76	-
182-350°C	22.7	25.7	1.5	1000	27	-
350-520°C	31.2	14.4	1.8	2200	17	0.5
520°C+	21.7		4.3	6200		
Coke	11.5					
(ii) Monagas 450°C+ Pitch (96)						
Feed	100.0		3.6	8000		16.3
Products						
Gas	10.1					
C_5-200°C	10.8	49.1	1.4	2200	98	-
200-380°C	12.7	20.5	3.1	3000	37	0.06
380-520°C	23.1	11.1	3.3	4400	28	1.7
520°C+	22.5	-8.9	3.8	10100		27.0
Coke	20.8					

a long technical development period would be needed before the process could be considered for a commercial plant.

(g) Production of Olefins

As discussed in Section 3.3.1, research has been done on a two stage pyrolysis process for the production of light olefins and aromatics from heavy oil and pitch feeds (63, 64). The first stage pyrolyzes the feed at 440°C to produce light products similar to those from the processes discussed above. These products were then cracked further at 700-800°C with a short residence time in the second stage to produce the desired light olefin products. The combination of high temperature, producing extensive cracking to short chain molecules, and short residence time, minimizing secondary condensation reactions, are required to produce olefins by pyrolysis.

Several process developers have worked on processes for production of olefins from whole crude and heavy oil feeds with some having reached commercial production. Some of these processes are:

(i) Lurgi Sand Cracker - same principle as process in Section 3.3.1 (f) with a sand heat carrier heated by supplemental fuel.

(ii) BASF Fluidized Coke Cracking - heat provided by partial combustion with oxygen of fluidized coke bed in the reactor.

(iii) BASF Fluidized Flow Cracking - heat generated in a separate regenerator.

(iv) Ube - partial combustion with oxygen in a fluidized bed.

(v) KK Heat Carrier Process - fluidized bed reactor using coke as the heat carrier.

(vi) Union Carbide Advanced Cracking Reactor - heat carrier is superheated steam produced by partial combustion.

(vii) Dow Process - heat carrier as in (vi).

(viii) Stone & Webster Thermal Regenerative Cracking (TRC) - solid heat carrier in a fluidized reactor.

(ix) Mitsui COSMOS Process - used molten salts as both heat carrier and catalyst to prevent coke formation.

(x) The Petroleum and Chemical Corp. Paccal Cyclic Thermal Cracking - atomized pitch sprayed onto hot refractory.

A detailed review of all these processes is beyond the scope of this study but is given in reference (100) which lists additional references. A summary of the process conditions and yields is in Table 3.12. Most of these results are with whole crude oil feeds and little work seems to have been done with 525°C+ pitch as a feed.

Because these are mostly development processes, few economic values or utility requirements have been published. Stone & Webster has shown that the TRC process can produce ethylene 7-9¢/kg more cheaply than a conventional coil cracker for feeds with specific gravities of 0.9-0.95. Since pitch cannot be cracked in a coil, a direct comparison cannot be done but Stone & Webster gives pitch as an acceptable feedstock whose advantage would be its low cost to the ethylene producer (101). Union Carbide has stated that the high Conradson carbon content of pitch and the low ethylene yields that result make their process uneconomic with heavy feeds (102). Economics and utility requirements will vary considerably with these processes using pitch feed but quantitative values have not been published.

(h) Hybrid Process

In the Hybrid Process, a slurry of coal in pitch is fed to a fluidized bed where it is pyrolyzed at 750-850°C and 3 MPa to produce a gas product and char (23). The char is then gasified with steam and oxygen in the lower part of the reactor. The product gas from the reactor is quenched for heat recovery, and scrubbed for removal of tar and acid gases from the product fuel gas. The process is at the pilot plant stage in Japan and yield, product quality, utility requirements and economic data have not been published. It is similar in general concept to CANMET's pyrolysis/gasification process.

TABLE 3.12

PRODUCTION OF OLEFINS FROM WHOLE CRUDE AND HEAVY OIL

	Average	Range
Cracking temperature, °C	825	740-1000
Residence time, seconds	0.5	0.015-1.7
Ethylene yield, mass percent	24.5	20-31.8
Propylene/ethylene mass ratio	0.42	0.19-0.56
Fuel oil or pitch/ethylene mass ratio	0.77	0.16-1.30

(i) Low Temperature Carbonization

The Low Temperature Carbonization (LTC) process was operated by Veba Oel with their VCC process (see Section 3.3.3 (d)) until 1964 and is now being reactivated. In this process, pitch is pyrolyzed in a rotary kiln producing gas and liquid products, and coke (103). No detailed information about the process has been published.

3.3.2 Catalytic Pyrolysis

The overall reaction during catalytic pyrolysis is the same as with non-catalytic pyrolysis discussed in Section 3.3.1.

$$\text{Pitch} \rightarrow \text{Gas Product} + \text{Liquid Product} + \text{Char}$$

Free radical chain reactions still occur but the catalyst acts to accelerate some of them which usually results in a faster reaction rate with a modified product slate. Problems result from the high metals and condensed aromatics contents of the pitch when using solid catalysts. The nickel and vanadium in the pitch deposit on the catalyst deactivating and blocking catalytic sites while catalyzing unwanted secondary dehydrogenation reactions with cracked products. The high molecular weight condensed aromatics result in a high coke yield which covers the catalyst particle.

The work of Sekhar and Ternan with non-catalyzed pyrolysis was reported in Section 3.3.1. They also studied pyrolysis of hydrocracked Athabasca bitumen pitch with a gamma alumina catalyst (62). For pyrolysis at 450°C for 2 hours, 38.8 mass percent of the pitch reacted with the catalyst compared to 29.2 mass percent without catalyst. The gas yield increased by 100 percent and the liquid yield by 17 percent when the catalyst was used. The gas compositions were similar in both cases while the liquid had a higher aromatic content with the catalyst. The catalyzed reaction was found to be first order with respect to the reactant throughout the entire pyrolysis.

Two stage pyrolysis without a catalyst for the production of olefins was discussed in Section 3.3.1. This work has been extended to two stage catalyzed pyrolysis for the production of gasoline and distillate feeds (104). The first stage is a non-catalyzed pyrolysis at 440°C, as before, where most of the metals and condensed aromatics in the feed were left in the char or pitch residue. They found the nickel in the first stage pyrolyzed oil product was 1/10 of that in the pitch feed while the vanadium was 1/30 of the feed level. In this case the second stage was a bed of silica-alumina catalyst operated at 450-480°C. The low coke yields compared to direct cracking of the heavy feeds proved that many of the coke precursors had been left with the residual char and pitch in the first stage. The second stage yields of gasoline, distillate oils and coke corresponded to those from direct catalytic cracking of a vacuum gas oil. Yields from bitumen, which were found to be low when producing olefins in the non-catalyzed two stage process, showed more gasoline and light fuel oil production than from a paraffinic crude oil. Since preferred catalytic cracker feeds for gasoline production are polycycloparaffins and monocyclic aromatics followed by monocycloparaffins, normal paraffins and dicyclic aromatics, bitumen which is composed of alicyclic and branched structures should produce more gasoline and fuel oil than a paraffinic feed.

Wen and Cain (105) have measured the pyrolysis of coal tar over a temperature range of 400-855°C in a reactor containing beds of various catalysts. The tar sample had the heavier fractions removed and did not contain the impurities discussed above that have a negative effect on catalysts. They found synthetic zeolites and a natural zeolite, chabazite, showed strong catalytic activity; 5A molecular sieves and natural erionite having small pore diameters were less active; clay minerals such as kaolinite, montmorillonite and Kieselguhr had similar activity to small pore size zeolites; and quartz particles were least reactive. They concluded that the factors required for catalytic effectiveness were an effective pore size greater than about 0.7 nm, a large internal surface area accessible to the tar vapour and a large number of strongly acidic sites.

Mochida et al (106, 107) have studied pyrolysis catalyzed by aluminum chloride which is an acidic catalyst. Orinoco vacuum residue was reacted at 600°C for 2 hours (107). The coke and gas yields were increased by the catalyst, and the coke and oil products were of higher purity since the catalyst accelerated the desulphurization and denitrogenation reactions. As much as 70% of the sulphur in the feed pitch was removed during pyrolysis using 30% aluminum chloride. As the amount of catalyst was increased the oil began production at lower temperature, the amount of oil product decreased, and the contents of sulphur, nitrogen and aromatics in the oil decreased. The gas produced without the catalyst had methane as the major constituent with considerable amounts of C_3 and C_4, however, the C_4 gas became dominant when the catalyst was used. They also studied acid catalyzed pitch upgrading at 230-300°C producing distilled oil yields of up to 25.9 mass percent from Orinoco pitch (106). The role of the aluminum chloride in both cases is to enhance the elimination of alkyl side chains which are cracked to distillate oils and gas. The low aromatic content of the product oil indicates that the aromatics in the pitch have been condensed by the catalytic action of the aluminum chloride. This condensation produces hydrogen which can react with the C-S bonds cleaved by the strong acid catalyst to produce H_2S. The nitrogen decrease may follow the same mechanism. The pyrolytic pitch residue is highly aromatic and would be a good needle coke feedstock except that it contains the aluminum chloride catalyst. The recovery and cost of the catalyst are the main problems in applying this process commercially.

Shimokawa et al (108) studied pitch carbonization at pressures of 0.1 to 10 MPa. At 0.1 MPa the use of a zinc chloride catalyst reduced the temperature at which coking began to occur rapidly by 100°C compared to the non-catalyzed reaction. At 3 and 10 MPa nitrogen pressures, there was no appreciable difference with zinc chloride as the pressure suppressed the catalytic reaction.

Moschopedis and Speight (109) reacted Athabasca asphaltenes in a solvent with ferric chloride, aluminum chloride, cupric chloride, or elemental halogen. The resulting condensed product contained up to 38 mass percent halogen and could be thermally pyrolyzed at 300°C to produce a good quality aromatic coke with low H/C ratio and less than 1 mass percent halogen content. Coking could be done at lower temperatures by using metal catalysts such as copper at 200-300°C or sodium at 80-110°C. They extended their work by treating the asphaltenes with oxygen or sulphur at 150-250°C to yield a condensed product containing little additional oxygen or sulphur. Thermal treatment of the condensed product at 200-300°C yielded a good quality coke. The reaction effected by the oxygen or sulphur was thought to be condensation between aromatic and aliphatic fragments with hydrogen removed by production of either water or hydrogen sulphide.

(a) Asphalt Residual Treating (ART)

The ART Process was developed by Engelhard Corporation and is licensed by M.W. Kellogg. The process was developed in commercial test units of 1110 and 1590 m^3/d capacity and an 8745 m^3/d unit is now being operated by Ashland Oil Co. at Catlettsburg, Kentucky. The process is called a selective vapourization, and fluidized demetallization and decarbonization process. The conditions are set to vapourize the lighter fractions in the feed so that less feedstock pyrolysis occurs than in other decarbonization processes.

A schematic flow diagram of the process is in Figure 3.17 (23). The equipment is similar to that used in fluid catalytic cracking but the operating conditions, contact time and type of fluidized solid differ. The fluidizable solid is called ARTCAT and is small spherical particles with low catalytic activity made of a proprietary calcined kaolin (110). The feedstock conversion to light components distilling below 350°C is considerably lower than with a fluid catalytic cracker. The reactor conditions have been given as 480-590°C and less than 0.45 MPa (110) but the riser contact time has not been published. Regenerated ARTCAT from the burner is mixed at the base of a very short contact time fluid riser system with residual pitch feed, recycle and fluidizing steam or water. The selective vapourization of the higher hydrogen content molecules in the asphaltic portion of the feed results in deposition on ARTCAT of essentially all of the metal containing components and a majority of the lowest hydrogen content hydrocarbon components and the nitrogen and sulphur in the feed. Commercial operation has shown the ART process will:

- remove essentially 100 percent of the asphaltenes and 80-90 percent of the Conradson carbon

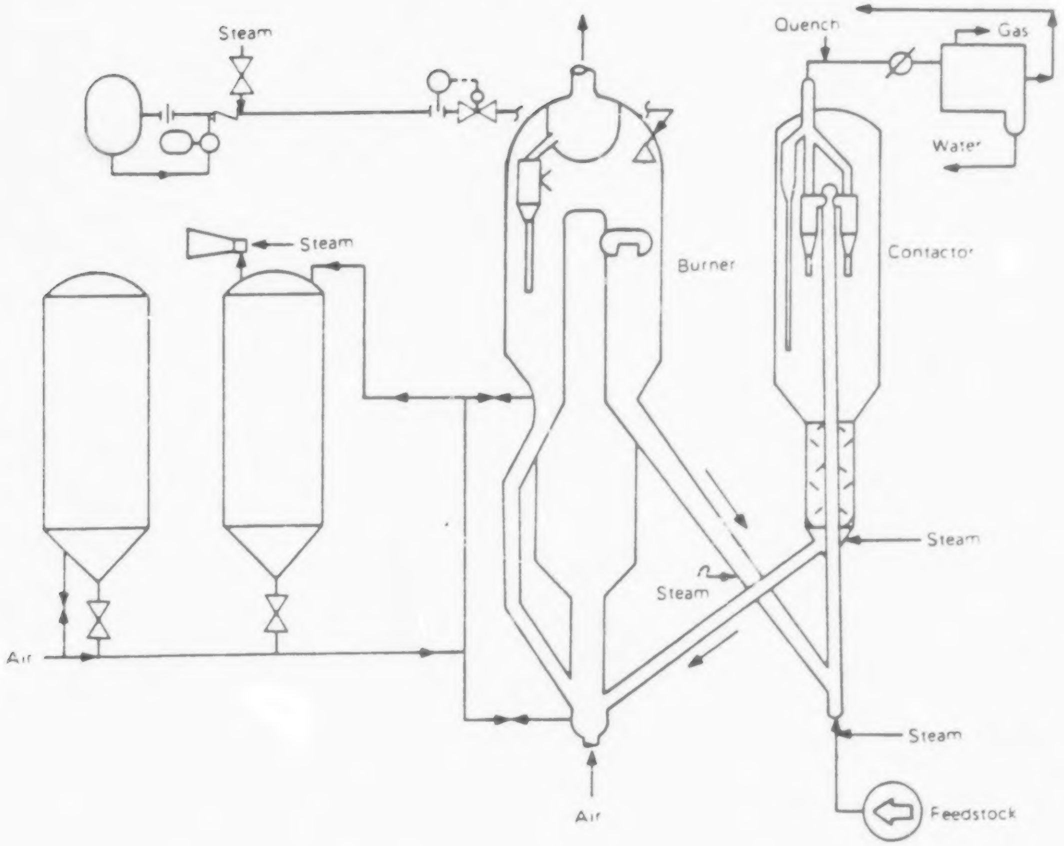
- remove 95+ percent of the metals, including sodium

- remove 35-75 percent of the nitrogen and sulphur

- convert most of the 525°C+ in the feed to lighter products.

FIGURE 3.17

ART PROCESS FLOW SCHEMATIC


Steam
Quench
Gas
Water
Steam
Burner
Contactor
Steam
Steam
Air
Steam
Air
Feedstock

The mechanism of these reactions has not been published. The product vapours are separated from the coke and metals laden ARTCAT by cyclones at the top of the riser. The vapours are quenched, cooled and separated into products in a fractionator.

The spent ARTCAT falls through a steam stripper for hydrocarbon removal and flows into the burner where the coke is burned with air in a fluidized bed. The heat generated raises the ARTCAT temperatures to provide the heat of reaction in the riser reactor. Excess heat can be removed from the burner by steam generation in coils within the bed, although tests with feeds having a Ramsbottom Carbon Residue as high as 12.5 mass percent showed that no burner heat removal was necessary even when practising complete CO combustion in the regenerator. The hot regenerated ARTCAT is then recycled back to the riser reactor. Some of the equilibrium ARTCAT must be purged from the system to remove the impurities deposited from the pitch, but ARTCAT can tolerate a much higher metals level than is possible with a fluid catalytic cracking zeolitic catalyst. The fresh ARTCAT addition rate will be less than 4.3 kg/m^3 at 100 mg/kg metals in the feed which is 5 to 10 times less makeup than would be required with a zeolitic catalyst. Engelhard has developed a process that recovers the nickel and vanadium from ARTCAT allowing the catalyst to be recycled to the ART unit.

Because of its relatively low conversion, the ART process has been considered as a pretreatment process for removal of catalyst poisons prior to more severe catalytic treatment in fluid catalytic cracking or hydroprocessing units. Yield and product quality data are shown in Table 3.13 for an atmospheric pitch and whole Athabasca bitumen feeds (23, 111). The heavy gas oil (HGO) contains a small amount of 525°C+ material which is of relatively high quality. Since it has a low

TABLE 3.13

ART PROCESS YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Watson K	Conradson Carbon Mass Percent
(i) Heavy Arabian Atmospheric Pitch (23)						
Feed	100.0	12.7	4.3		11.5	13.3
Products						
C_2-	3.0					
C_3-C_5	3.1					
Gasoline	13.0	51.6	0.4		11.6	
LGO	15.0	27.5	1.4		11.4	
HGO+	55.3	11.4	4.3		11.4	
Coke	10.6					
(ii) Whole Athabasca Bitumen (111)						
Feed	100.0	8.0	4.8	3900	11.2	12.9
Products						
C_4-	7.2					
C_5-193°C	7.2	52.0	0.5		11.6	
LGO	23.3	26.2	1.7	1140	11.1	
HGO+	51.5	9.1	4.3		11.1	6.6
Coke	10.8					

asphaltene content and H/C ratio similar to that of the feed, it can be processed with the HGO in conventional refinery HGO processing units.

Capital cost and utility consumptions for processing 7950 m^3/d of Heavy Arabian reduced crude are in Table 3.14 (23). Other capital cost and utility data have been given (111, 112) but they include downstream units processing ART products and the costs for the ART unit alone cannot be separated. Kellogg has developed costs for a plant to upgrade 11,900 m^3/d of Athabasca bitumen to a 34° API synthetic crude. They calculated a total operating cost, exclusive of feedstock cost and capital considerations, of \$7.90/m^3 of bitumen. The capital cost for the complete plant was estimated at \$300 million (U.S.) on an Alberta construction basis (111).

(b) Heavy Oil Cracking (HOC)

Heavy Oil Cracking is essentially fluid catalytic cracking with some pitch mixed with the standard vacuum gas oil feed. The process configuration is basically the same as the ART process but the catalyst used is a high activity zeolite that results in high conversion of the feed to products in the gasoline and light distillate oil range. Since these catalysts are very sensitive to contaminants in the feed, such as metals, nitrogen and carbon residue, the process cannot normally be used directly with the types of pitch considered in this study. A pretreatment step is required before HOC processing. UOP has presented the data in Table 3.15 (113) which breaks different feedstock properties into categories of HOC processing difficulty. As the pitch properties in Section 4.0 show, most of the 525°C+ pitches being evaluated in this study are in Type III and cannot be fed directly to an HOC. Ashland has presented data from a plant using the ART process to pretreat HOC feed (114), Gulf has discussed the use of residue hydrodesulphurization (see Section 3.3.3 (a)) to remove contaminants from pitch prior to fluid catalytic cracking (115), and Air Products and Chemicals has proposed using the H-Oil process (see Section 3.3.3 (b)) to pretreat HOC feed (116).

Total (117) has developed an HOC process to convert the Type II feeds shown in Table 3.15 while Phillips (118) has operated on HOC on Type I and II fees for over twenty years.

TABLE 3.14

ART PROCESS ECONOMICS

(i) Capital Cost, $U.S. per m^3/d pitch capacity	8800
(ii) Utilities Consumption, per m^3 feed	
Steam, 3.1 MPa	390 kg
Cooling water, 10°C ΔT	14 m^3
Process water	0.1 m^3

TABLE 3.15

PITCH FEEDSTOCK CLASSIFICATIONS FOR HOC

Type	Catalytic Cracking Processability	Properties		
		°API	Metal mg/kg	Conradson Carbon Mass Percent
I	Relatively easy	> 20	<15	<4
II	Difficult	15-20	15-80	4-10
III	Requires pre-processing	<15	>80	> 10

UOP (113, 119) has presented residual catalytic cracking data with Type I and II feeds. A great deal of work has been done in developing catalysts that are more resistant to the metals in residue feeds (120) and additives that passivate the metals (121). Since the process has not been applied to the pitches of interest in this study, a full review is outside the scope of this report. The basics of the process are as presented for the ART process and the references listed above can be referred to for more information.

(c) Heavy Oil Treating Process (HOT)

This is a process at the 40 m^3/d pilot plant stage for catalytically cracking pitch, while simultaneously producing hydrogen, in a fluidized bed or iron ore particles. The process is being developed in Japan by Nippon Mining Co., Hitachi, Kashima Oil Co. and RAROP (23). A flowsheet of the process is in Figure 3.18 (23). The pitch feed is catalytically pyrolyzed to light and middle distillates at 514°C and 0.3 MPa in the cracker. The ferrous oxide in the catalyst is converted to Fe_3O_4 by steam to generate hydrogen that reacts with hydrocarbon free radicals to minimize condensation reactions and can be used for subsequent product hydrotreating. The cracker reactions are:

$$\text{Pitch} + Fe_3O_4 \longrightarrow \text{Liquid product} + \text{gas product} + \text{coke}/Fe_3O_4$$

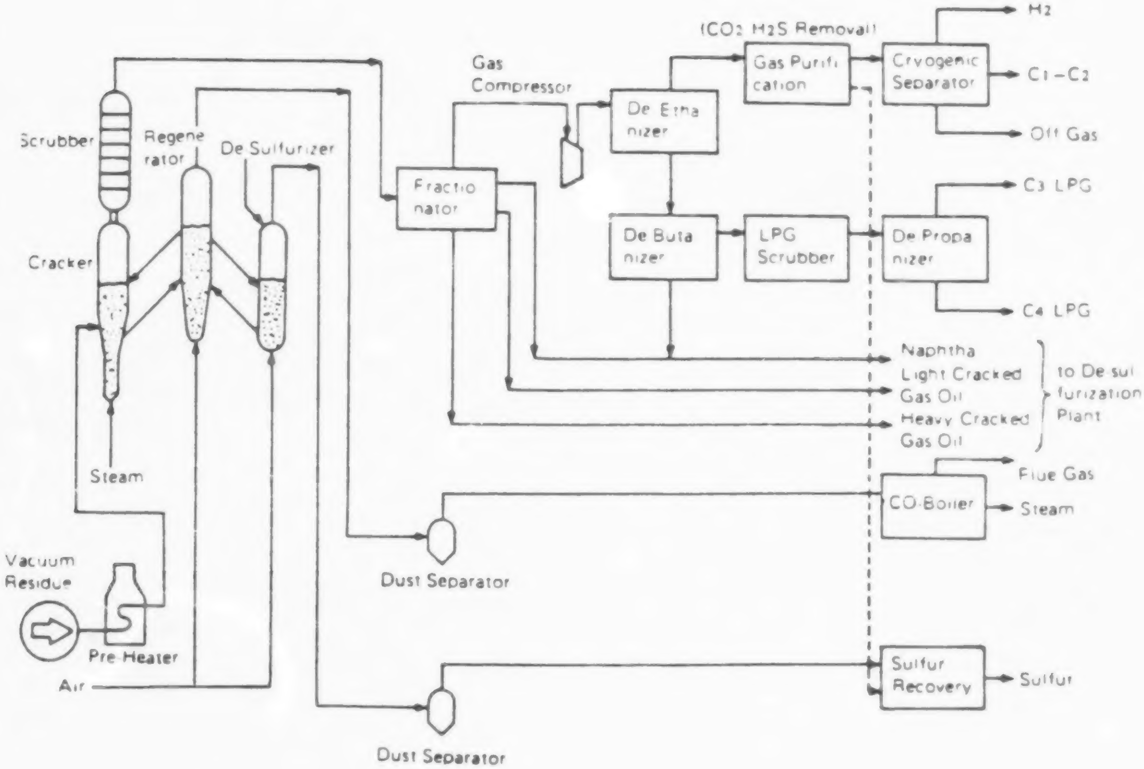
$$3FeO + H_2O \longrightarrow Fe_3O_4 + H_2$$

The unconverted feed is condensed in the scrubber and recycled to the reactor. The vapour products flow to a fractionator for product separation.

In the regenerator, the coke deposited on the catalyst is burned to carbon monoxide at 830°C. The heat is used for the process reactions and the carbon monoxide reduces the Fe_3O_4 returning to the cracking reactor. The sulphur in the coke forms SO_2 on combustion which reacts with the iron oxide resulting in a low SO_2 concentration in the flue gas. The reactions are:

FIGURE 3.18

HEAVY OIL TREATING PROCESS FLOW SCHEMATIC


(CO2 H2S Removal)
H2
Gas Purification
Cryogenic Separator
C1 – C2
Gas Compressor
De Ethanizer
Off Gas
Scrubber
Regenerator
De Sulfurizer
Fractionator
C3 LPG
Cracker
De Butanizer
LPG Scrubber
De Propanizer
C4 LPG
Naphtha
Light Cracked Gas Oil
Heavy Cracked Gas Oil
to De sulfurization Plant
Steam
Flue Gas
CO Boiler
Steam
Vacuum Residue
Dust Separator
Pre Heater
Sulfur Recovery
Sulfur
Air
Dust Separator

$$\text{Coke}/Fe_3O_4 + O_2 \longrightarrow 3FeO + CO + CO_2$$

$$FeO + SO_2 + 3CO \longrightarrow FeS + 3CO_2$$

Some of the catalyst from the regenerator flows to the desulphurizer, a third reaction vessel, where the iron sulphide reacts with air at 750°C to produce a gas with SO_2 concentration high enough for subsequent sulphur recovery. The reaction is:

$$3FeS + 5O_2 \longrightarrow Fe_3O_4 + 3SO_2$$

The desulphurized catalyst then returns to the regenerator.

The process has shown a relatively high yield of middle distillates as shown by the data in Table 3.16 for pitch from an Arabian Light crude (23).

Because this is a development process, no utility or economic data have been published.

3.3.3 Hydrogen Addition

The hydrogen addition processes are an extension of the pyrolysis processes discussed above with a high hydrogen partial pressure imposed on the basic pyrolysis reactions. The important reactions that occur are hydrocracking, desulphurization, denitrogenation and demetallation which all result in greater asphaltene conversion. These reactions may be simply represented by:

Hydrocracking	$R\text{-}R + H_2 \rightarrow 2RH$
Desulphurization	$RSH + H_2 \rightarrow RH + H_2S$
Denitrogenation	$RN + 2H_2 \rightarrow RH + NH_3$
Demetallation	$RMR + 1/2\ H_2 \rightarrow RH + RM$

The reactions can be done non-catalytically but more often a catalyst is used to increase the reaction rate, product selectivity and conversion. The process must allow for the catalyst deactivation that results from the deposition of coke and inorganic material on the catalyst which becomes more severe with heavier pitches. Catalysts are chosen on the grounds of activity, selectivity and life with combinations of the sulphides of cobalt, molybdenum, nickel and tungsten, all supported on alumina, being widely used for hydrotreating.

TABLE 3.16

HEAVY OIL TREATING PROCESS YIELDS

Feed: Light Arabian Vacuum Pitch

Products	Volume Percent
C_2-	9.0
C_3-C_4	7.6
C_5-180°C	15.2
180-230°C	8.2
230-360°C	14.2
360-510°C	28.2
	82.4

Where hydrodesulphurization is the major reaction, catalysts based on cobalt molybdate are usually chosen. For hydrocracking or hydrodenitrogenation a stronger, more acid catalyst such as nickel molybdate or nickel tungstate may be used. Basic components released during denitrogenation can act to neutralize strong acid catalyst sites although at normal operating temperatures this has not been a problem.

Typical operating conditions for the hydrogen addition processes are:

Temperature	300 - 500°C
Pressure	5 - 20 MPa
Gross hydrogen flow	350 - 3500 Nm^3/m^3 oil
Net chemical hydrogen consumption	35 - 350 Nm^3/m^3 oil
Catalyst life	Up to about 1 year

The main reaction variables affecting conversion are temperature, pressure and space velocity (time) and there is much greater flexibility to vary these parameters and change the reaction severity or conversion than there is with thermal pyrolysis processes. Conversions of pitch to light products ranging from 30-90 percent can be achieved by different processes (52).

The hydrocracking reactions involve thermal pyrolysis as discussed in Section 3.3.1 followed by acid catalyzed hydrogenation to prevent the coke forming condensation reactions from occurring. A simplified mechanism was shown as Route 1 in Figure 3.8 with hydrogen acting to stabilize free radicals formed during cracking of C-C bonds. A higher H/C ratio in the aromatic constituents of thermally hydrocracked pitch is attributed to stabilization of aromatic radicals by hydrogen (60). Under typical reaction conditions, the hydrogenation reactions are competing with the pyrolysis condensation, or coke forming, reactions. Therefore, in order to minimize coke formation and catalyst deactivation, the hydrogen partial pressure is kept high and the temperature is as low as possible. As the conversion of 525°C+ pitch increases above 60 percent, the residual hydrocracked pitch becomes incompatible with the lighter hydrocracked products and precipitates. The reason for this is the same as discussed with visbreaking in Section 3.3.1 (a).

As noted in Section 3.3.1, the C-S bond is weak making both aliphatic and heterocyclic sulphur the easiest species to remove during hydrogen addition. This results in free radical formation by the sulphur containing asphaltenes, which are stabilized by hydrogen, forming smaller sized molecules. Because of the large excess of hydrogen, double bond and aromatic saturation can occur at the same time.

Denitrogenation requires more severe conditions than desulphurization. This is because the bond holding the nitrogen atom to the aromatic ring is strong and the reaction proceeds through aromatic ring saturation and cleavage before the nitrogen is removed.

The vanadium and nickel metals are in solution in the feed oil as porphyrins (Figure 3.5) or are maintained in solution in asphaltene micelles as discussed in Section 3.3.1 (a). Under reaction conditions the organic chain associated with the metal is cracked and stabilized by hydrogen. This cracking reduces the solubility of the remaining organo-metal complex and leads to precipitation of metals on or downstream of the catalyst. Since the deposition of metals can lead to rapid catalyst deactivation, a low cost, expendable catalyst is used in some cases (52).

Ng et al (122) found a single approximate linear relationship between catalytic desulphurization and asphaltene conversion for pitches from Athabasca, Canadian Blend, Light Arabian and Cold Lake oils. A different linear relationship was found for pitch from Boscan crude. This is attributed to the high metal content, particularly vanadium, in the Boscan pitch and indicates that vanadium removal is an important path for asphaltene conversion in Boscan pitch. A model is referenced in which the destruction of micelles by vanadium removal and the depolymerization of asphaltene molecules by desulphurization are the major pathways for the conversion of asphaltene (122).

The hydrocracking of Athabasca bitumen using catalysts of MoO_3 - CoO on three supports with significantly different pore diameters was studied by Ternan (123) at 400°C and 13.9 MPa. He found that higher conversions were obtained with higher surface area catalysts having smaller pore diameters even though pore diffusion controlled the rate of reaction.

Nomura et al (124) hydrocracked Athabasca asphaltene over molten salts at 400°C and 9.8 MPa initial hydrogen pressure in a batch reactor for 1 h. A melt of $ZnCl_2$ - KCl - NaCl resulted in yields of 23 mass percent gas, 62 mass percent liquids and 15 mass percent coke. Addition of CuCl to the melt slightly increased the coke yield while addition of $NiCl_2$ slightly decreased it. Addition of $MoCl_5$ to the melt resulted in only 4 mass percent coke yield and an increase in asphaltene conversion from 90 to 99 mass percent.

In the remainder of this section some of the hydrogen addition processes available for producing lighter products from 525°C+ pitch are reviewed. A brief process description, typical yield and product quality data, and economic parameters, when available, are presented. The reaction mechanisms have been discussed above and are not repeated with each process.

(a) Resid Hydrodesulphurization

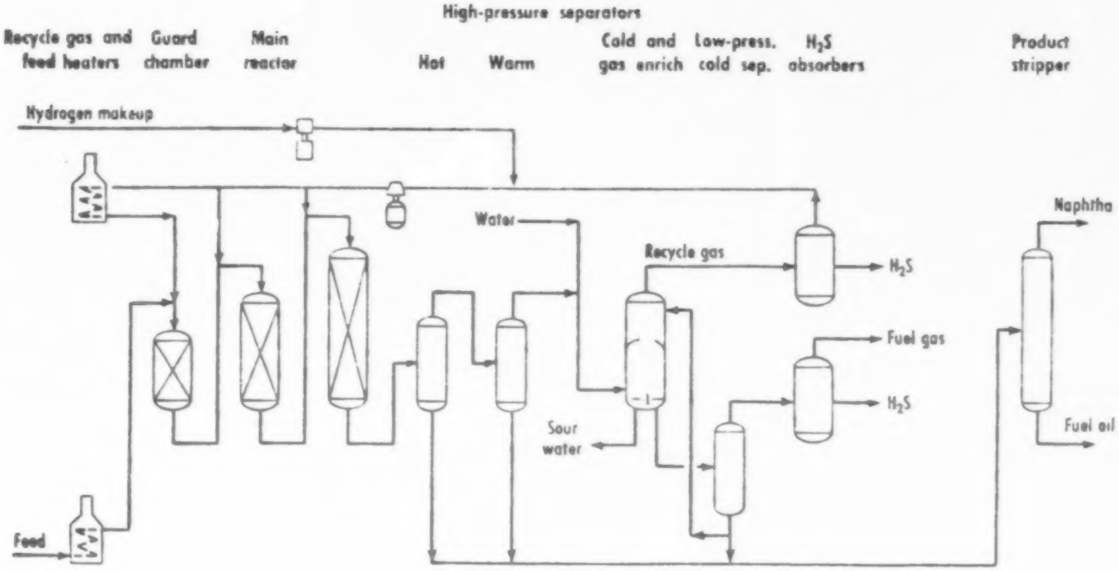
Residual oil hydrodesulphurization (resid HDS) processes have evolved from the light distillate HDS processes that are widely used. The process is licensed by several different developers including Chevron, Exxon, UOP, Union and Shell. The processes operate with a fixed bed of catalyst and the main problem in applying them to date has been the frequent catalyst replacement that is required due to metals and coke deposition on the catalyst when using pitch feeds.

A typical flowsheet for the process is in Figure 3.19. Fresh feed is heated and mixed with recycle hydrogen at 400-450°C and 10-20 MPa for feed to the reactors. An initial guard bed reactor containing an inexpensive catalyst may be used for metals removal prior to the main catalytic reactors. All of the reactors contain fixed beds of catalyst sized for an LHSV of 0.1 to 1.0 flow volumes/h/reactor volume. The gas/liquid product from the last reactor flows to the product recovery section of the plant which consists of a series of high and low pressure separators with final fractionation. The hydrogen rich gas is treated for hydrogen sulphide removal and is then recycled to the reactors.

As its name implies, the process was initially developed for sulphur removal from fuel oil and since the C-S bond is the easiest to break, a design based on sulphur removal will have a limited conversion with 525°C+ pitch conversions typically

FIGURE 3.19

RESID HYDRODESULPHURIZATION PROCESS FLOW SCHEMATIC


High-pressure separators
Recycle gas and feed heaters
Guard chamber
Main reactor
Hot
Warm
Cold and gas enrich
Low-press. cold sep.
H_2S absorbers
Product stripper
Hydrogen makeup
Water
Recycle gas
H_2S
Naphtha
Fuel gas
H_2S
Fuel oil
Sour water
Feed

Ref: Union Oil Co., Oil & Gas Journal, pg. 67, February 7, 1977.

in the 20-50 percent range. Yield and product quality data for three feeds are in Table 3.17 (4, 23). Since the products are mainly in the 340°C+ range, the process is used as a feed pretreatment step prior to a higher conversion process when the pitch is to be converted to lighter products. Chevron (125) has discussed developments in resid HDS catalysts. They showed that the use of a tailored non-cylindrical catalyst rather than a standard cylindrical catalyst doubled the 525°C+ pitch conversion from 20 to almost 40 percent.

Shell is developing a related process called HDM/HCON that solves the problem of high metals content feeds by using a regenerable hydrodemetallization catalyst which is replaced during operation in the first stage of the process (126). The catalyst replacement is accomplished in a moving bed or bunker flow reactor. The conversion (HCON) part of the process is then carried out in typical fixed bed resid HDS reactors using tailored Shell catalysts. With Athabasca bitumen, Shell claims the process can achieve demetallization of 95 mass percent, desulphurization of 92 mass percent, asphaltene conversion of 90 mass percent and 525°C+ pitch conversion of 68 mass percent which are higher than can be achieved with standard resid HDS processes. The Athabasca bitumen pitch feed properties and yields are in Table 3.18.

Investment and utility consumption data for the heavy Arabian and Lloydminster resid HDS cases in Table 3.17 are given in Table 3.19 (4).

(b) H-Oil

The H-Oil process was developed over 20 years ago by Hydrocarbon Research Inc. (HRI) and Cities Service Oil Co. They later decided not to continue collaborating on the process and the process development was continued by HRI who were later joined by Texaco Development Corp. Husky Oil has recently acquired an ownership position with rights to license the process in Canada.

TABLE 3.17

RESID HYDRODESULPHURIZATION YIELDS AND PROPERTIES

		Volume Percent	°API	S, Mass Percent	Ni+V mg/kg	H_2 Consumption Nm^3/m^3
(i)	Light Arabian Vacuum Pitch (23)					
	Feed	100.0	6.5	4.1		134
	Products					
	C_5-343°C	5.7				
	343-538°C	18.1				
	343°C+	96.5		1.0		
	538°C+	78.4		1.2		
(ii)	Heavy Arabian Vacuum Pitch (4)					
	Feed	100.0	5.1	5.3	198	196
	Products					
	C_5-191°C	2.9				
	191-343°C	9.7				
	343°C+	90.1	14.8	1.0	41	
(iii)	Lloydminister Atmospheric Pitch (4)					
	Feed	100.0	10.6	4.4	246	200
	Products					
	C_5-191°C	2.5				
	191-343°C	22.0				
	343°C+	79.4	19.0	0.35	14	

TABLE 3.18

HDM/HCON YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Ni+V mg/kg	H_2 Consumption Nm^3/m^3
(i) Athabasca Bitumen 524°C+ Pitch (126)						
Feed	100.0	0.6	5.85	5000	539	330
Products						
IBP-204°C	8.0	39.3	20 mg/kg	16		
204-343°C	17.2	25.8	0.013	430		
343-524°C	35.6	19.6	0.12	1200		
524°C+	32.3	9.3	1.29	6200	62	

TABLE 3.19

RESID HYDRODESULPHURIZATION ECONOMICS

	Heavy Arabian Vacuum Pitch	Lloydminster Atmospheric Pitch
(i) Capital Cost 1984 \$U.S./m^3/d pitch feed	14,800	21,400
(ii) Utilities Consumption, per m^3 pitch feed		
Electricity, kWh	59	60
Steam, 4.2 MPa & 399°C, kg	(26)	(26)
Steam, 0.45 MPa & sat'd, kg	117	86
Fuel, MJ	504	504
Cooling water, 11°C ΔT, m^3	4.6	4.8
Boiler feed water, m^3	0.07	0.07

( ) Amount produced

The basic process flowsheet is in Figure 3.20 (23) and is very similar in general concept to the resid HDS flowsheet in Figure 3.19. The main differences are the reactor type and the use of the hydrocracked product pitch as a recycle stream.

The process takes place in ebullated bed reactors, shown in Figure 3.21 (116), which are essentially 3-phase fluidized bed reactors. The pitch feed and hydrogen gas are mixed hot and fed to the bottom of the reactor where they flow up through a distributor plate into the fluidized reaction zone. The velocity in the reactor is held high enough to fluidize the catalyst by use of an ebullating pump which recycles liquid through the reactor. The ebullated bed operates almost isothermally and eliminates the possibility of plugging or blockage from buildup of coke or sediment as is possible with the fixed bed HDS reactors. Onstream addition and withdrawal of catalyst allows a steady catalyst activity to be maintained and eliminates the periodic shutdowns for catalyst replacement that are necessary with fixed beds. Two or more reactors can operate in series, the first acting with a less expensive catalyst to demetallize the feed. The reactor is very flexible, allowing a wide range of product yields and properties to be attained by changes in catalyst, temperature, pressure and residence time (LHSV).

A significant process improvement that resulted from HRI's involvement in the H-Coal program was the recycle of the hydrocracked product pitch back to the reactor to increase the conversion. This also allows a lower reactor severity relative to once-through operation at the same conversion, resulting in reduced gas yields and hydrogen consumption. HRI has found that the use of vacuum bottoms recycle with a heavy Arabian 525°C+ pitch feed gave the following changes (116):

525°C+ pitch conversion	+20.0 volume percent
Conradson carbon conversion	+18.6 mass percent
Chemical hydrogen consumption	+64 Nm^3/m^3
C5-175°C naphtha product	+ 4.3 volume percent
175-340°C distillate product	+ 6.8 volume percent
340°C+ bottoms product	- 9.8 volume percent

The commercial H-Oil units are all operating on once-through mode at 55-70 volume percent conversion of the pitch feed. Because of the advantages shown above at 85-90 volume percent conversion with vacuum bottoms recycle, HRI is working to

FIGURE 3.20

H-OIL PROCESS FLOW SCHEMATIC

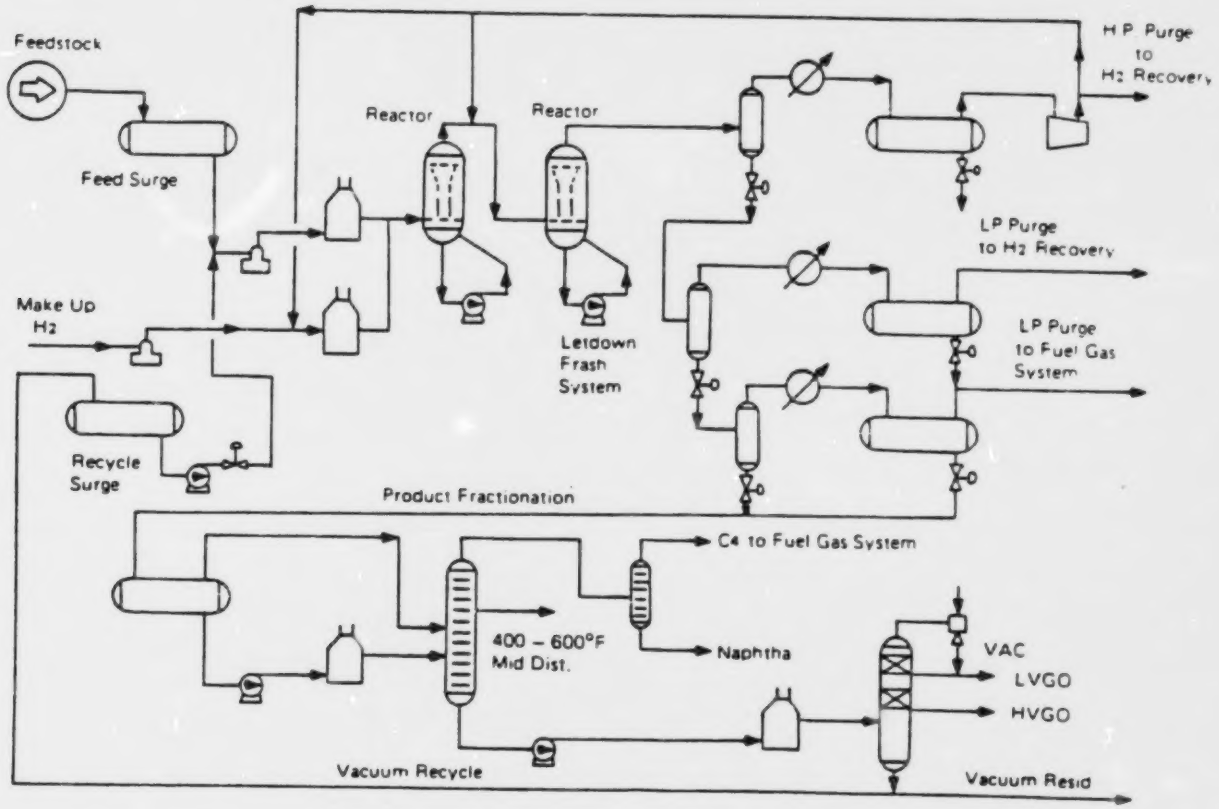
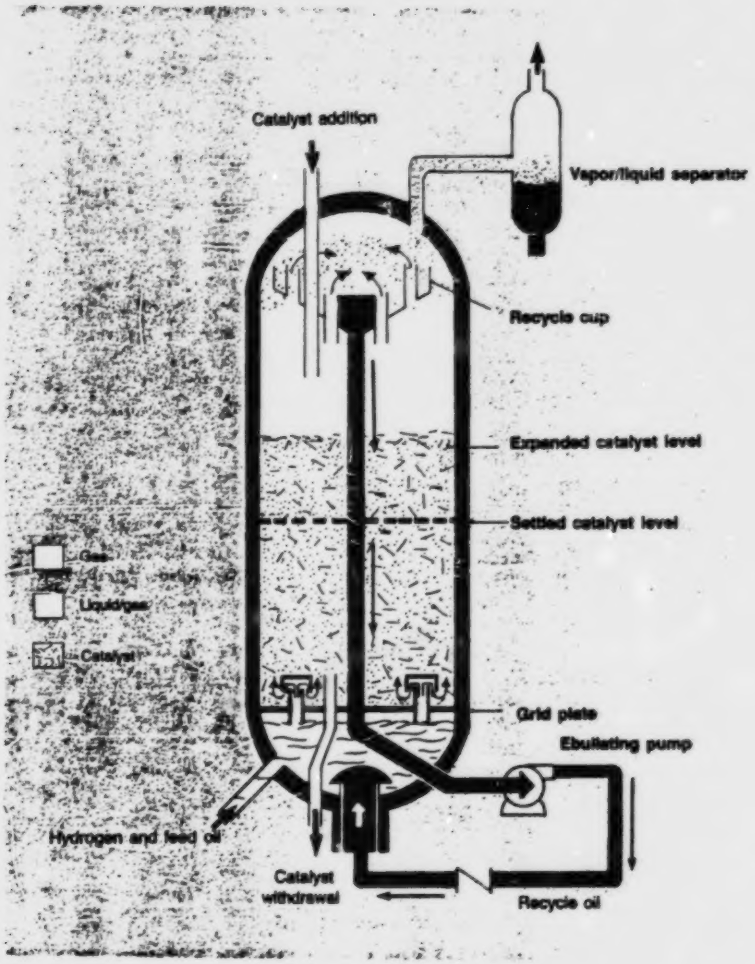

Feedstock
Feed Surge
Reactor
Reactor
H.P. Purge to H_2 Recovery
LP Purge to H_2 Recovery
Make Up H_2
Letdown Frash System
LP Purge to Fuel Gas System
Recycle Surge
Product Fractionation
C4 to Fuel Gas System
400 – 600°F Mid Dist.
Naphtha
VAC
LVGO
HVGO
Vacuum Recycle
Vacuum Resid

FIGURE 3.21

EBULLATED BED REACTOR


Catalyst addition
Vapor/liquid separator
Recycle cup
Expanded catalyst level
Settled catalyst level
Gas
Liquid/gas
Catalyst
Grid plate
Ebullating pump
Hydrogen and feed oil
Catalyst withdrawal
Recycle oil

demonstrate this operation on a commercial scale. One disadvantage of the recycle mode of operation is that the cracked pitch product is not compatible with the lighter product oils and must be disposed of separately. This is for the same reasons as discussed with visbreaker pitch in Section 3.3.1 (a).

Yields and product properties from low and high conversion operation with Arabian, Athabasca bitumen and Cold Lake pitch feeds are in Table 3.20 (4, 116, 127, 128).

Investment and utility consumptions required for vacuum bottoms recycle operation on light Arabian vacuum pitch are in Table 3.21 (4).

(c) LC-Fining

After their separation with HRI, Cities Service continued separate development of the ebullated bed process with Lummus under the process name of LC-Fining. Amoco Oil Co. has since joined in the development of the technology. In spite of the separate development, the basic process concept and reactor configuration are the same as shown in Figures 3.20 and 3.21 and discussed in Section 3.3.3 (b). Lummus has recently developed a new system for separating the reactor effluent products at low pressure rather than at the conventional high pressure. They claim that this results in an investment saving of 20-25 percent and will be operated for the first time as part of Syncrude's current expansion program (129).

The use of vacuum bottoms recycle is a patented HRI concept and Lummus has promoted lower conversions in the 75 volume percent range. Two sets of typical yields are in Table 3.22 (4, 23). The concept of low conversion LC-Fining or H-Oil followed by coking of the product pitch may be more attractive now than the high conversion process since it was selected for both the Syncrude and Husky projects.

Estimated investment and utilities consumption values are in Table 3.23 (4). As with the previous investment values given, this value is of doubtful use because its basis is not clearly defined.

TABLE 3.20

H-OIL YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Ni+V mg/kg	H_2 Consumption Nm^3/m^3
(i) Light Arabian 524°C+ Pitch (4) (90 volume percent 524°C+ pitch conversion)						
Feed	100.0	6.5	4.4	3500		221
Products						
C_3-	8.6					
C_4-204°C	18.3	64	0.2	150		
204-343°C	26.0	33	0.9	670		
343-524°C	38.2	18	1.9	3070		
524°C+	10.7	-3	3.2	7210		
(ii) Heavy Arabian 524°C+ Pitch (116) (90 volume percent 524°C+ pitch conversion)						
Feed	100.0	4.9	5.6	4270	228	300
Products						
C_4-	12.5					
C_5-177°C	13.7					
177-343°C	29.8					
343°C+	46.6					
(iii) Heavy Arabian 343°C+ Pitch (116) (65 volume percent 524°C+ pitch conversion)						
Feed	100.0	12.6	4.3	2700	125	174
Products						
C_4-	3.8					
C_5-177°C	10.7					
177-343°C	30.6					
343°C+	51.5					

TABLE 3.20 (Cont'd)

H-OIL YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Ni+V mg/kg	H_2 Consumption Nm^3/m^3
(iv) Whole Athabasca Bitumen (127) (60 volume percent 524°C+ pitch conversion)						
Feed	100.0	8.3	4.9	4500	325	96
Products						
C_4-	6.2					
C_5-221°C	12.9					
221-524°C	59.5					
524°C+	22.2					
(v) Whole Athabasca Bitumen (127) (92 volume percent 524°C+ pitch conversion)						
Feed	100.0	8.3	4.9	4500	325	151
Products						
C_3-	8.3					
C_4-193°C	15.9	59.0	0.65	450		
193-510°C	71.9	19.6	2.42	3100		
510°C+	5.2	-9.5	5.50	17000		
(vi) Cold Lake 399°C+ Pitch (128) (85 volume percent 524°C+ pitch conversion)						
Feed	100.0	6.9	5.15	4611	333	215
Products						
C_4-	9.3					
C_5-177°C	11.2	60.9	0.17	270		
177-343°C	25.9	33.2	0.69	1450		
343-524°C	44.3	17.7	1.65	3740	< 2	
524°C+	11.1	-2.6	3.12	10140	360	

TABLE 3.21

H-OIL ECONOMICS

(i) Capital Cost

1984 U.S. Gulf Coast, \$U.S. per m^3/d pitch capacity	21,400

(ii) Utilities Consumption, per m^3 feed

Fuel	438 MJ
Electricity	69 kWh
Cooling water (11°C ΔT)	1.6 m^3
Catalyst, 1984 U.S. \$/m^3	3.90

Basis: Feed at 343°C, makeup hydrogen at 2.2 MPa

TABLE 3.22

LC-FINING YIELDS AND PROPERTIES

	Volume Percent	°API	S, Mass Percent	H_2 Consumption Nm^3/m^3
(i) Light Arabian 525°C+ Pitch (23) (75 volume percent 525°C+ pitch conversion)				
Feed	100.0		3.9	236
Products				
C_3-	8.0 (mass)			
C_4-200°C	21.5			
200-350°C	30.5			
350-525°C	29.4			
525°C+	25.0		1.2	
C_4+	106.4	27.5		
(ii) Heavy Arabian 524°C+ Pitch (4) (65 volume percent 524°C+ pitch conversion)				
Feed	100.0	4.6	5.6	281
Products				
C_4-204°C	16.5			
204-343°C	19.4			
343-524°C	35.7			
524°C+	35.0			
C_4+	106.6	23.7	0.75	
(iii) Lloydminster/Cold Lake Blend 343°C+ Pitch (4, 129) (65 volume percent 524°C+ pitch conversion)				
Feed	100.0	6.5	5.0	207
Products				
C_5-204°C	15.2	56.0	0.05	
204-343°C	23.7	30.5	0.20	
343-524°C	40.9	19.8	0.60	
524°C+	24.1	3.4	2.20	
C_4+	105.6	23.0	0.85	

TABLE 3.22 (Cont'd)

LC-FINING YIELDS AND PROPERTIES

		Volume Percent	°API	S, Mass Percent	H_2 Consumption Nm^3/m^3
(iv)	Lloydminster/Cold Lake Blend 343°C+ Pitch (129) (85 volume percent 524°C+ pitch conversion)				
	Feed	100.0	6.5	5.0	295
	Products				
	C_5-204°C	25.7	56.0	0.05	
	204-343°C	39.9	30.5	0.35	
	343-524°C	29.5	17.5	1.10	
	524°C+	10.3	-4.5	3.30	
	C_5+	105.4	27.6	0.87	
(v)	Athabasca Bitumen 204°C+ (129) (65 volume percent 524°C+ pitch conversion)				
	Feed	100.0	6.6	5.2	171
	Products				
	C_5-204°C	15.6	53	0.10	
	204-343°C	29.6	32	0.95	
	343-524°C	38.6	16	1.95	
	524°C+	19.1	-1	4.50	
	C_5+	110.8	22	2.00	

TABLE 3.23

LC-FINING ECONOMICS

	Heavy Arabian 524°C+ Pitch	Lloydminster/ Cold Lake 343°C+ Pitch
(i) Capital Cost 1984 U.S. Gulf Coast \$U.S. per m^3/d feed capacity	16,600	12,600
(ii) Utilities Consumption, per m^3 feed		
Fuel, MJ	376	387
Electricity, kWh	78	50
Steam (1.1 MPa), kg	(89)	(87)
Cooling water, m^3	2.9	1.8
Catalyst, 1984 U.S. \$/m^3	3.46	4.09

(   ) Amount produced

(d) Veba-Combi-Cracking (VCC)

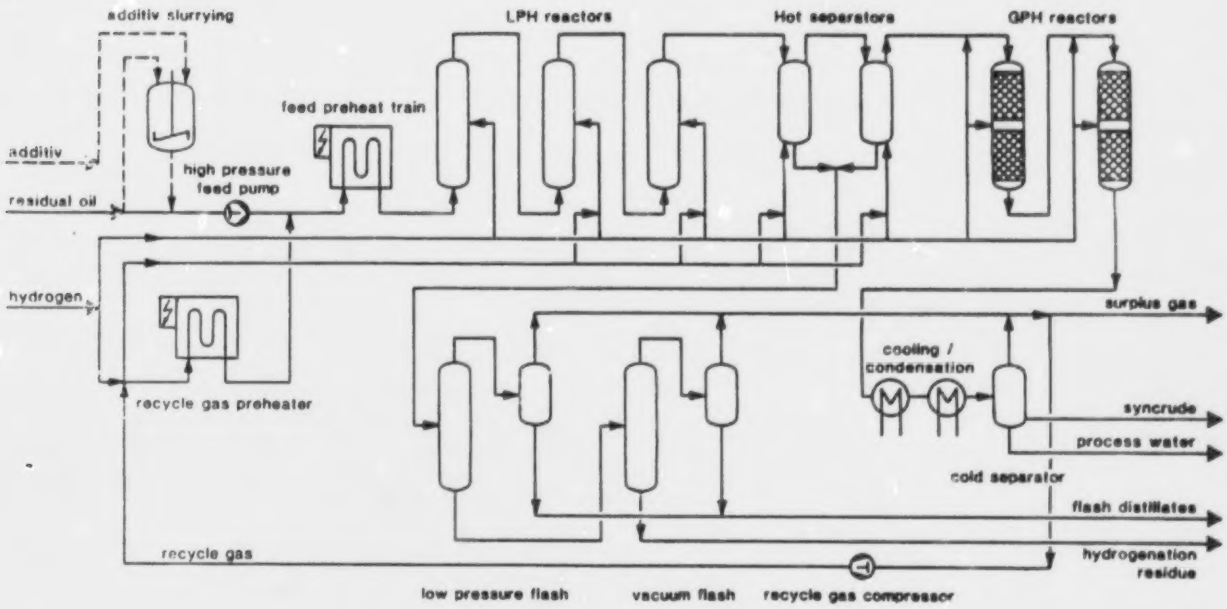
The Veba-Combi-Cracking (VCC) process has developed from work on coal liquefaction that was begun by Bergius in 1913. Plants using this technology to produce liquid fuels from coal operated in Germany until 1945. In 1952 the process was used for residual oil conversion in a two-stage operation that became the VCC process. These plants were shutdown in 1964 for economic reasons but in 1977 further development of the technology began after petroleum prices had risen. In 1983 a 1 t/h pilot plant for heavy oil and pitch conversion began operation. The process is being developed and licensed by Veba Oel Development of West Germany.

A process flowsheet is in Figure 3.22 (130). The pitch feed is mixed with 1-3 mass percent of an optional additive before the reactors. Details about the additive or the criteria for determining when it is needed have not been published. The additive is a once through catalyst that flows through with the reactants and ends up in the hydrogenated pitch residue. The pitch and optional additive mix with hot, hydrogen-rich recycle gas and are heated further before entering the liquid phase hydrogenation (LPH) reactors. These are open, cylindrical upflow reactors with no internals that operate at 440-480°C and 15-30 MPa. This upper pressure is about 10 MPa higher than the pressure at which the hydrogen addition processes discussed earlier operate. The reaction occurs in a cascade of LPH reactors with quench gas added for temperature control and the residual liquid and vapour product are separated at pressure in the hot separators. Since the hot separator liquid contains the residual pitch, the LPH reactors determine the VCC process conversion. Conversions up to 98 percent have been achieved on a bench scale unit and 95 percent on the 1 t/h pilot plant. The pilot testing has achieved this conversion with the pressure reduced from 28 to 18 MPa which is more in line with other hydrogen addition processes.

The vapour product from the hot separators and the flash distillates are processed further in the gas phase hydrogenation (GPH) reactors over standard fixed bed catalysts. This results in high quality naphtha and distillate products which can make a high quality synthetic oil from the product cold separation or fractionation. Most of the hydrogen rich product gas is recycled to the LPH reactors.

FIGURE 3.22

VEBA-COMBI-CRACKING PROCESS FLOW SCHEMATIC


additiv slurrying
LPH reactors
Hot separators
GPH reactors
feed preheat train
additiv
high pressure feed pump
residual oil
hydrogen
recycle gas preheater
surplus gas
cooling / condensation
syncrude
process water
cold separator
flash distillates
recycle gas
hydrogenation residue
low pressure flash
vacuum flash
recycle gas compressor

The temperature, pressure and residence time can be varied with this process to give a broad range of conversion levels (65-98 mass percent) and product properties but Veba has discussed primarily high conversion operation. A set of yields and product properties from processing Athabasca bitumen are in Table 3.24 (103) showing that the process produces naphtha suitable for reforming, middle distillate of diesel quality and vacuum gas oil for fluid catalytic cracking or hydrocracking. Because of the high conversion and product quality, the VCC hydrogen consumption at 2-4 mass percent on feed is about double the consumption of the H-Oil or LC-Fining processes.

There has been very little published on capital costs and utilities for this process. The only capital cost value had no definition and is, therefore, of no use. The only utilities reported were for a bitumen fractionation and upgrading case and are (131):

Natural gas	1740 MJ/m^3 bitumen
Boiler feed water	0.6 m^3/m^3 bitumen
Electricity	120 kWh/m^3 bitumen

(e) CANMET Hydrocracking

The CANMET Hydrocracking process is very similar in concept to the LPH portion of the VCC process discussed in the previous section. The process has been developed by CANMET at their Energy Research Laboratory and is now being commercialized and licensed by Petro-Canada working in conjunction with Partec Lavalin Inc. A schematic process flowsheet is in Figure 3.23 (132). The pitch feed mixes with about 1 mass percent additive and a hydrogen rich gas before entering the reactor. The reactor is an open cylinder with no internals that operates upflow. The overhead product stream is separated for recovery of light hydrocarbon products, unconverted pitch and recycle gas. The additive used is a low cost, once through composition of pulverized coal impregnated with ferrous sulphate or other salts (132). The additive suppresses coke formation and allows the process to achieve pitch conversions of 90+ percent at pressures of 10-14 MPa which is lower than other hydrocracking processes at the same conversion (133, 134). Reaction temperatures have not been published but are likely to be similar to the range given for the VCC process. Metals are deposited on the additive during the pitch cracking reaction and are removed in the pitch product from either the

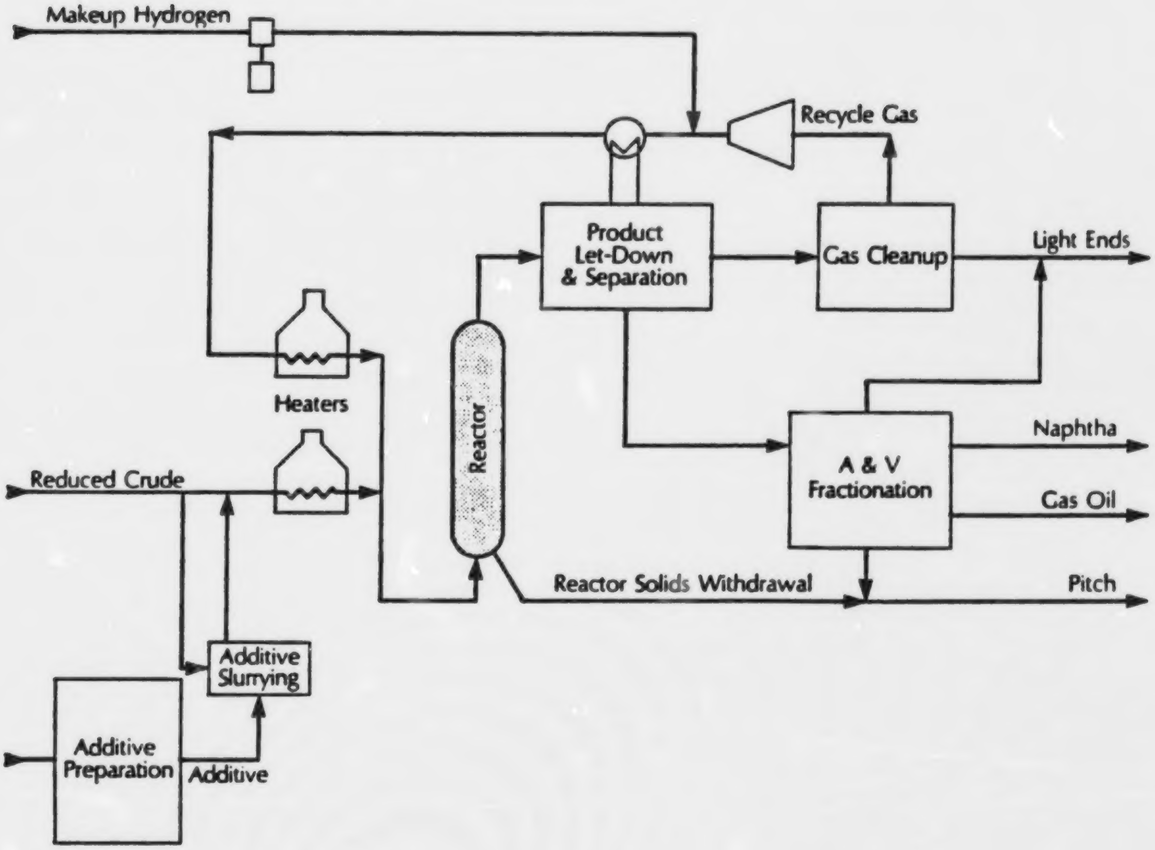
TABLE 3.24

VEBA-COMBI-CRACKING YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Ni+V mg/kg	H_2 Consumption Nm^3/m^3
Whole Athabasca Bitumen (103) (95 mass percent 510°C+ pitch conversion)						
Feed	100.0	8.2	5.0	5000	342	360
Products						
C_4-	12.5					
C_5-200°C	19.0	54.7	< 1 mg/kg	< 1		
200-350°C	37.0	31.1	< 20 mg/kg	< 5		
350-500°C	32.0	22.3	< 50 mg/kg	< 10	< 1	
500°C+	3.0					

FIGURE 3.23

CANMET HYDROCRACKING PROCESS FLOW SCHEMATIC


Makeup Hydrogen
Recycle Gas
Product Let-Down & Separation
Gas Cleanup
Light Ends
Heaters
Reactor
A & V Fractionation
Naphtha
Gas Oil
Reduced Crude
Reactor Solids Withdrawal
Pitch
Additive Slurrying
Additive Preparation
Additive

reactor overhead or a solids withdrawal stream from the reactor.

Process yields and product qualities are shown in Table 3.25 for both a light Arabian pitch and Athabasca bitumen. The light Arabian case is the design basis for the 795 m^3/d demonstration plant at Petro-Canada's Montreal refinery.

The only economic data published are in Table 3.26 (4).

(f) Asphaltenic Bottom Cracking (ABC)

The Asphaltenic Bottom Cracking (ABC) process is being developed by Chiyoda Chemical Engineering & Construction Co. Ltd. The process has not yet been demonstrated commercially.

The process concept is similar to that of fixed bed hydrodesulphurization presented in Section 3.3.3 (a) and shown in Figure 3.19. The main difference is the ABC catalyst which is a proprietary cylindrical extrudate about which no details have been published. This fixed bed catalyst is resistant to coke fouling and metal deposition even when treating pitches with high asphaltene and metals levels. The process has a lower hydrogen consumption than a commercial HDS catalyst at the same conversion. The proposed mechanism is the depolymerization by breaking alkyl-aromatic bonds and C-S bonds in alkyl chains along with the destruction of asphaltene micelles by vanadium removal. The condensed ring asphaltene structure is not changed resulting in products in the heavy distillate boiling range.

Chiyoda has proposed using the process as a pretreatment step before a standard HDS reactor or integrated with a solvent deasphalting (SDA) unit with the SDA asphalt recycled back to the ABC reactor to extinction (23).

The reported operating conditions are at the low severity end of the range of conditions given for other hydrogen addition processes (135):

Pressure	9 - 18 MPa
Temperature	360 - 430°C
LHSV	0.2 - 1.5 h^{-1}

TABLE 3.25

CANMET HYDROCRACKING YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Conradson Carbon Mass Percent	H_2 Consumption Nm^3/m^3
(i) Light Arabian 552°C+ Pitch (132) (85 mass percent 552°C+ pitch conversion)						
Feed	100.0	7.4	4.3	2600	22.3	191
Products						
C_3-	8.7					
C_4-204°C	18.2	57.8	0.16	300		
204-343°C	27.6	31.0	1.8	1100		
343-524°C	32.4	14.1	2.7	3400	1.0	
524°C+	14.8	-19.5	4.3	7800	63.5	
(ii) Athabasca Bitumen 524°C+ Pitch (132) (92 mass percent 524°C+ pitch conversion)						
Feed	100.0	0	6.2	6800	27.9	
Products						
C_1-C_3	7.9					
C_4-204°C	32.2)					
204-343°C	36.1)	Volume Percent				
343-524°C	29.2)					
524°C+	7.7)					
(iii) Athabasca Bitumen 269°C+ (132)						
Feed	100.0	8.1	4.7	4200	14.9	
Products						
C_1-C_3	5.0					
C_4-204°C	28.9)					
204-343°C	44.3)	Volume Percent				
343-524°C	26.6)					
524°C+	4.1)					

TABLE 3.26

CANMET HYDROCRACKING ECONOMICS

(i) Capital Cost

1984 U.S. Gulf Coast, $U.S. per m^3/d feed capacity	23,900

Total installed cost for light Arabian 525°C+ pitch including additive preparation but excluding downstream fractionation.

(ii) Utilities Consumption, per m^3 pitch feed

Fuel	1060 MJ
Electricity	67 kWh
Steam (4.2 MPa)	80 kg
Cooling Water (22°C ΔT)	1.4 m^3
Additive	11.4 kg

ABC process yields with Athabasca bitumen and Khafji (heavy Arabian crude) vacuum pitch are in Table 3.27 (135). The results show relatively mild conversion and confirm that the process should be considered as a pretreatment step prior to a higher severity process. The results with extinction recycle of SDA asphalt are also shown in Table 3.27 (135, 136). They show lower product metals, asphaltene and sulphur levels compared to the once-through ABC process, and would be suitable feeds for a standard refinery fluid catalytic cracker or hydrocracker.

The only economic and utility consumption data published are in Table 3.28 (23). The plant investment was derived for a Japanese location for the ABC/SDA integrated case.

(g) Aurabon

The Aurabon process is a fixed bed catalytic process that is similar in concept to the resid hydrodesulphurization and ABC processes discussed in earlier sections. It is being developed by UOP Inc. and has not yet been commercially proven.

The process was originally developed as a pretreatment step to remove metals and asphaltenes prior to more conventional refinery processes such as hydrodesulphurization, fluid catalytic cracking or hydrocracking (137). The process arrangement is similar to the ABC/SDA process discussed in Section 3.3.3 (f). The reactor separation section produces a recycle stream that is cracked to extinction, a slate of standard refinery cuts and a small waste pitch stream to remove asphaltenes and metals from the process. The original process fed atmospheric pitch and operated at low severity achieving 98 percent demetallization, 98 percent asphaltene reduction, 60 percent Conradson carbon reduction, 30-40 percent desulphurization but only 35 percent conversion of the 565°C+ pitch in the feed.

The process has been developed further by UOP to increase the conversion level and improve the economics of the process. The process now feeds vacuum pitch but the basic configuration of the reactor and separation sections are unchanged. Details about these sections have not been published and the operating conditions of the reactor are said to be similar to resid hydrodesulphurization processes. The improved version achieves 85 percent conversion of the 565°C+ pitch in the

TABLE 3.27

ASPHALTENIC BOTTOM CRACKING YIELDS AND PROPERTIES

(i) ABC Alone (135)	Athabasca Bitumen		Khafji Vacuum Pitch	
Asphaltene conversion, percent	78		49	
Demetallization, percent	80		71	
Desulphurization, percent	59		40	
H_2 consumption, Nm^3/m^3	100		92	
	Feed	Product	Feed	Product
°API	9.2	16.4	5.1	11.6
Conradson carbon, mass percent	13.5	7.3	23.6	16.8
Sulphur, mass percent	4.4	1.8	5.3	3.2
Ni + V, mg/kg	254	52	236	68

(ii) ABC with SDA Recycle (135, 136)	Athabasca Bitumen		Khafji Vacuum Pitch	
	Feed	Product	Feed	Product
°API	9.6	18.2	5.1	18.9
Conradson carbon, mass percent	13.6	4.9	23.6	4.6
Sulphur, mass percent	4.6	2.0	5.3	1.6
Nitrogen, mg/kg	4400	4000		2600
Ni + V, mg/kg	268	8	236	0.5

TABLE 3.28

ASPHALTENIC BOTTOM CRACKING ECONOMICS

(i) Capital Cost

1982 Japanese location, $U.S. per m^3/d feed capacity (23) Cost for ABC/SDA combined process	31,500

(ii) Utilities Consumption, per m^3 pitch (23)

Fuel	1250 MJ
Electricity	68 kWh
Steam (medium pressure)	112 kg
Cooling Water	12.9 m^3
H_2 consumption	112-167 Nm^3

feed, 99+ percent demetallization, 98+ percent asphaltene reduction, 85+ percent Conradson carbon reduction, 60-70 percent desulphurization from a Boscan 565°C+ pitch feed. In spite of the higher conversion, the product still contains 78 wt percent 340°C+ fraction and will require further processing for a significant yield of transportation fuels (138).

Economic data published for the high conversion process with Boscan 565°C+ pitch feed are in Table 3.29 (138).

(h) Donor Refined Bitumen (DRB)

The Donor Refined Bitumen (DRB) process has been developed by Gulf Canada Ltd. based on previously developed donor solvent coal liquefaction technology. The essence of the process is the pyrolysis of the pitch feed in an operation similar to visbreaking (Section 3.3.1 (a)) but in the presence of an efficient hydrogen donor which stabilizes the intermediates formed during the pitch pyrolysis. Because the process can be used in the difficult operating conditions of an oil sands plant, a key factor in Gulf's decision to develop the process has been its perceived ease of operability and forgiveness resulting from the relative simplicity of the chemistry, the process and the equipment (56). The process has not yet been proven commercially.

A schematic flowsheet of the process is in Figure 3.24 (139). Pitch mixes with the liquid donor before the reaction heater. The donor is composed primarily of saturated and unsaturated, single and double ring aromatic compounds. The heater and reactor contain no catalyst and are similar to the heater and soaking drum in Shell's visbreaking process where the reactor is a vessel to give the required residence time for the reactions to occur. Reaction conditions are 410-460°C and 4.1 to 5.5 MPa. The pressure is set to keep the donor in the liquid phase and no hydrogen overpressure is required resulting in a pressure less than half that of the gaseous hydrogen addition processes discussed in earlier sections. The hydrogen transfer in the cracking reactor occurs by the tetralin in the donor losing hydrogen to cracked intermediates and becoming naphthalenes. The reaction product goes through a typical separation and fractionation system with the depleted donor recovered from a sidestream on the atmospheric fractionator. The naphthalenes in the depleted donor are converted back to tetralin by hydrogen addition in a fixed bed

TABLE 3.29

AURABON PROCESS ECONOMICS

(i) Capital Cost

1984 U.S. Gulf Coast, $U.S. per m^3/d feed capacity Includes product fractionation	19,200

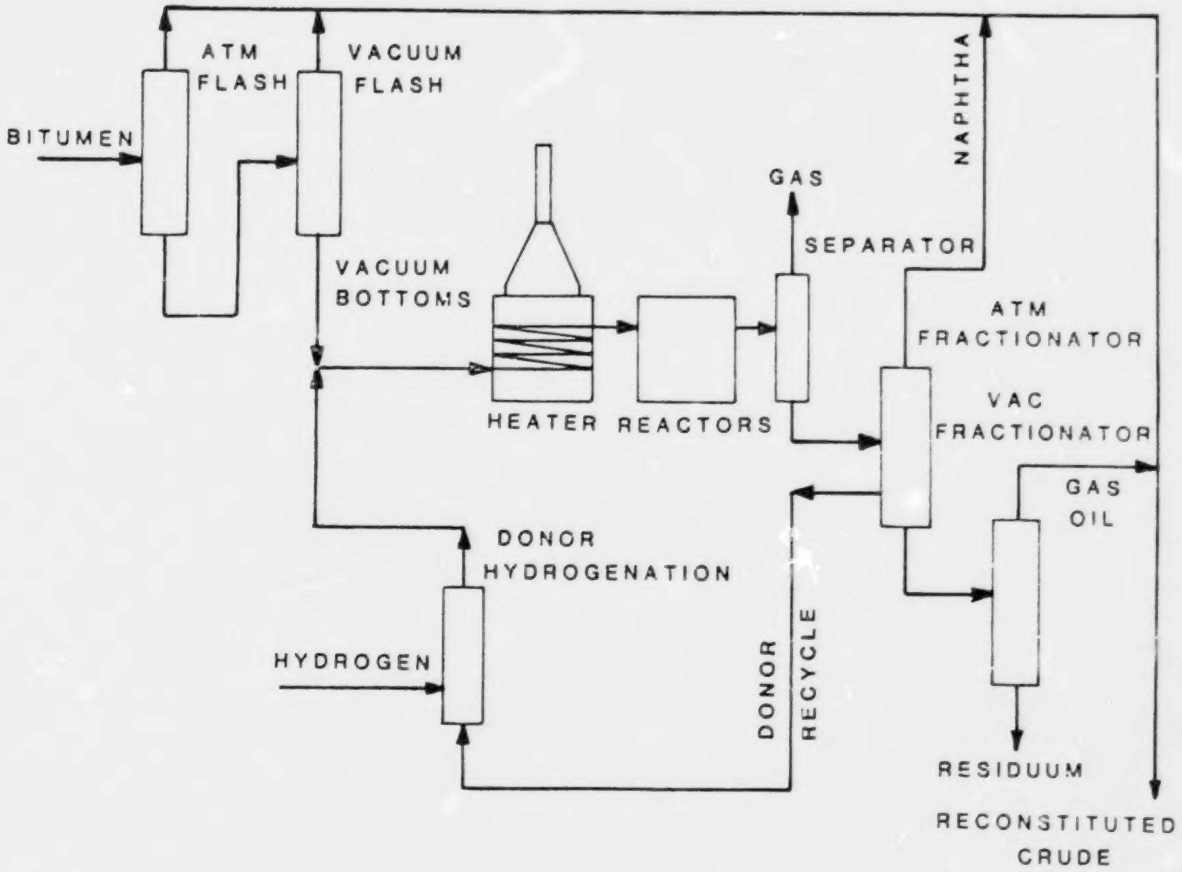
(ii) Utilities Consumption, per m^3 pitch feed

Fuel	358 MJ
Electricity	85 kWh
Steam, high pressure	(43 kg)
Steam, medium pressure	(143 kg)
Steam, low pressure	(40 kg)
Boiler feed water	0.3 m^3
Cooling water	0.6 m^3

( ) Amount produced

FIGURE 3.24

DONOR REFINED BITUMEN PROCESS FLOW SCHEMATIC


ATM
FLASH
VACUUM
FLASH
BITUMEN
NAPHTHA
GAS
SEPARATOR
VACUUM
BOTTOMS
ATM
FRACTIONATOR
HEATER
REACTORS
VAC
FRACTIONATOR
GAS
OIL
DONOR
HYDROGENATION
HYDROGEN
DONOR
RECYCLE
RESIDUUM
RECONSTITUTED
CRUDE

catalytic reactor. This reaction occurs at conventional HDS temperature and pressure but a high LHSV. The hydrogen added when converting Athabasca bitumen pitch is about 120 m^3/m^3 of pitch feed. The donor:pitch ratio used at those conditions is 2:1 (56, 139, 140).

The process has achieved conversions of the 525°C+ pitch feed of 65-70 mass percent. Yields from Athabasca bitumen pitch and a western Canadian crude pitch are given in Table 3.30 (139, 140). Product properties are given in detail in both references. The cracked product pitch content is higher than with many of the more severe, high conversion processes discussed above but Gulf feels that the operability and forgiveness of the process, compared to the higher severity ones, compensates for this yield disadvantage.

The capital cost of a plant converting 3660 m^3/d of Athabasca bitumen pitch has been estimated by Gulf at \$20,500 U.S./m^3/d (139). This cost includes direct material, direct field labour, indirect costs, contractor's fee and contingency and is U.S. Gulf Coast based in 1983 U.S. dollars. The equipment cost includes vacuum distillation, DRB reactors and donor separation, hydrogenation and storage but excludes the hydrogen plant, amine unit, sulphur plant, and feed/product storage. Gulf expects the DRB cost to be lower than hydrocracking process costs due to the low pressures and high space velocities that are used.

Operating costs were estimated at \$55.30 U.S./m^3 of Athabasca pitch feed including labour and maintenance, utilities, depreciation, interest on investment, insurance and taxes (139).

3.4 Pitch Gasification

The processes considered in this section react pitch with oxygen and steam to produce carbon monoxide and hydrogen in a mixture commonly called synthesis gas because of the many different chemicals that can be made from it. In principle, any hydrocarbon may be synthesized and possible reactions are shown below with the more important reactions summarized in Figure 3.25 (52):

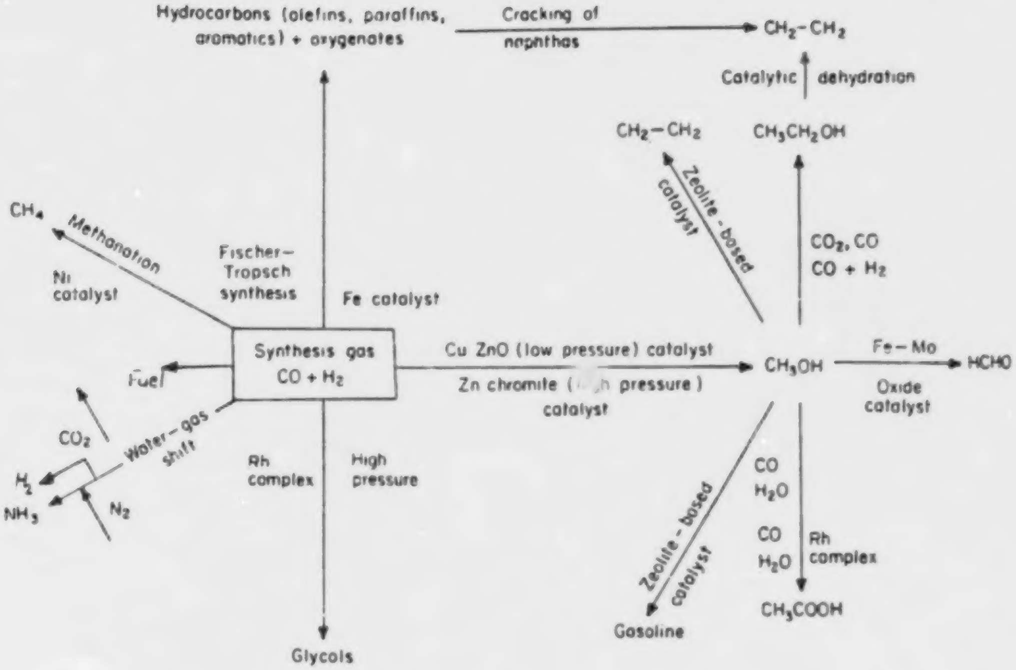
TABLE 3.30

DRB PROCESS YIELDS AND PROPERTIES

	Mass Percent	°API	S, Mass Percent	N mg/kg	Ni+V mg/kg	Conradson Carbon Mass Percent
(i) Western Canadian 500°C+ Pitch (139)						
Feed	100.0	12.1	0.92	4870	31	18.4
	Conversion Low - High					
Products						
C_3-	6.6 - 8.1					
C_4-190°C	26.1 - 43.7	45.6	0.1	92		
190-360°C	0					
360-504°C	34.8 - 23.6		0.6	3500		
504°C+	32.5 - 24.6	-14.1	1.5	10300	68	52.3
(ii) Athabasca Bitumen 500°C+ Pitch (139, 140)						
Feed	100.0	1.9	6.9	6550	481	23.2
Products						
C_3-	5.2					
C_4-190°C	23.7	51.1	0.9	130		
190-360°C	7.7					
360-504°C	30.0					
504°C+	33.1	-10.9	6.1	12600	1541	47.7

FIGURE 3.25

SYNTHESIS GAS PROCESSING OPTIONS


Hydrocarbons (olefins, paraffins, aromatics) + oxygenates
Cracking of naphthas
CH_2-CH_2
Catalytic dehydration
CH_2-CH_2
CH_3CH_2OH
Zeolite - based catalyst
CO_2, CO
CO + H_2
CH_4
Methanation
Ni catalyst
Fischer–Tropsch synthesis
Fe catalyst
Synthesis gas
CO + H_2
Cu ZnO (low pressure) catalyst
Zn chromite (high pressure) catalyst
CH_3OH
Fe–Mo
Oxide catalyst
HCHO
Fuel
CO_2
Water-gas shift
H_2
NH_3
N_2
Rh complex
High pressure
Glycols
CO
H_2O
CO
H_2O
Rh complex
CH_3COOH
Zeolite - based catalyst
Gasoline

Alkanes	$(n+1)H_2 + 2nCO = C_nH_{2n+2} + nCO_2$ $(2n+1)H_2 + nCO = C_nH_{2n+2} + nH_2O$
Alkenes	$nH_2 + 2nCO = C_nH_{2n} + nCO_2$ $2nH_2 + nCO = C_nH_{2n} + nH_2O$
Alkynes	$(n-1)H_2 + 2nCO = C_nH_{2n-2} + nCO_2$ $(2n-1)H_2 + nCO = C_nH_{2n-2} + nH_2O$
Alcohols	$2nH_2 + nCO = C_nH_{2n+2}O + (n-1)H_2O$
Aldehydes/ ketones	$2(n-1)H_2 + nCO = C_nH_{2n}O_2 + (n-2)H_2O$
Acids	$(2n-2)H_2 + nCO = C_nH_{2n}O_2 + (n-2)H_2O$

The reactions to ammonia and especially methanol are of most importance with much work having been done recently on processes leading to transportation fuels. Lutz (27) presented data for production of 1800 t/d of methanol by pitch gasification showing that the costs are competitive with the more conventional production route of steam reforming natural gas. It is beyond the scope of this study to consider the synthesis gas processing reactions in more detail. Other uses for the gas are for hydrogen production and as fuel.

Processes are being developed that gasify pitch by pyrolyzing it in the presence of hydrogen (52, 141). The reaction products vary with the reaction conditions but are typically light hydrocarbon gases and aromatics. The processes operate at 3-5 MPa and 755-785°C. Since these processes are not at the commercial development stage, they will not be reviewed in this section.

3.4.1 Non-Catalytic Gasification

The non-catalytic gasification of pitch occurs by reaction with oxygen and superheated steam. The main reactions are (142):

$$C_nH_m + \left(\frac{n}{2}\right)O_2 \rightarrow nCO + \left(\frac{m}{2}\right) H_2 \qquad (1)$$

$$C_nH_m + nH_2O \rightarrow nCO + \left(\frac{m}{2} + n\right) H_2 \qquad (2)$$

Thermal cracking occurs by

$$C_nH_m \rightarrow nC + \left(\frac{m}{2}\right) H_2 \qquad (3)$$

resulting in free carbon or soot that must be removed from the product gas. The free carbon can react by the relatively slow secondary reactions:

$$C + CO_2 \rightleftarrows 2CO \qquad (4)$$

$$C + H_2O \rightleftarrows CO + H_2 \qquad (5)$$

The normal residence time, however, is insufficient for these reactions to reach equilibrium and soot production can be up to 3 mass percent of feed with a heavy pitch.

Other reactions occurring are:

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \rightleftarrows nCO_2 + \left(\frac{m}{2}\right) H_2O \qquad (6)$$

$$C_nH_m + nCO_2 \rightleftarrows 2nCO + \left(\frac{m}{2}\right) H_2 \qquad (7)$$

$$C_nH_m + \left(\frac{m}{4}\right)O_2 \longrightarrow nC + \left(\frac{m}{2}\right) H_2O \qquad (8)$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad (9)$$

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \qquad (10)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (11)$$

Equation (1) is a combination of equations (6), (7) and (2). The above reactions are, of course, a simplification since the actual reactions are free radical in nature and the individual reactions involved are numerous.

Shell has suggested (143) that the reaction occurs in three phases. The first is a heating and cracking phase in which the hydrocarbon is vapourized and dispersed into oxygen and steam. The gas mixture is heated by radiation from the flame and the reactor walls and some cracking of the hydrocarbon to carbon, hydrogen, methane and hydrocarbon radicals occurs.

The second or reaction phase begins when the hydrocarbon is hot enough to react by (6). This equilibrium is far to the right so that all the oxygen is consumed. At flame temperature reactions (2) and (7) occur rapidly resulting in little net production of CO_2 or H_2O. Reactions (2) and (7) are endothermic and prevent reactor overheating by limiting the overall gas temperature to 1300-1500°C.

The third or soaking phase occurs beyond the flame front but still at high temperature where secondary reactions (9), (10), (4) and (5) take place. The final product gas composition is determined by the equilibrium conditions of (11) at the 1250-1300°C outlet temperature. Some steam is usually fed to the reactor to moderate the flame temperature. There is considerable flexibility to control the product gas composition by changing the steam dosage along with the oxygen:fuel ratio. Within normal operating limits, the reactor pressure has only a small effect on the product gas composition.

The oxygen for the gasification reactions would be provided as a high purity stream except in the case when the product gas was being used as fuel when air could be used. The fuel gas produced by oxygen gasification is a medium heating value gas of about 11.2 MJ/m^3 while that produced by air gasification is a low heating value gas of about 3.7 MJ/m^3. Since the low heating value gas has only a limited application it is not considered in the discussion of individual processes below.

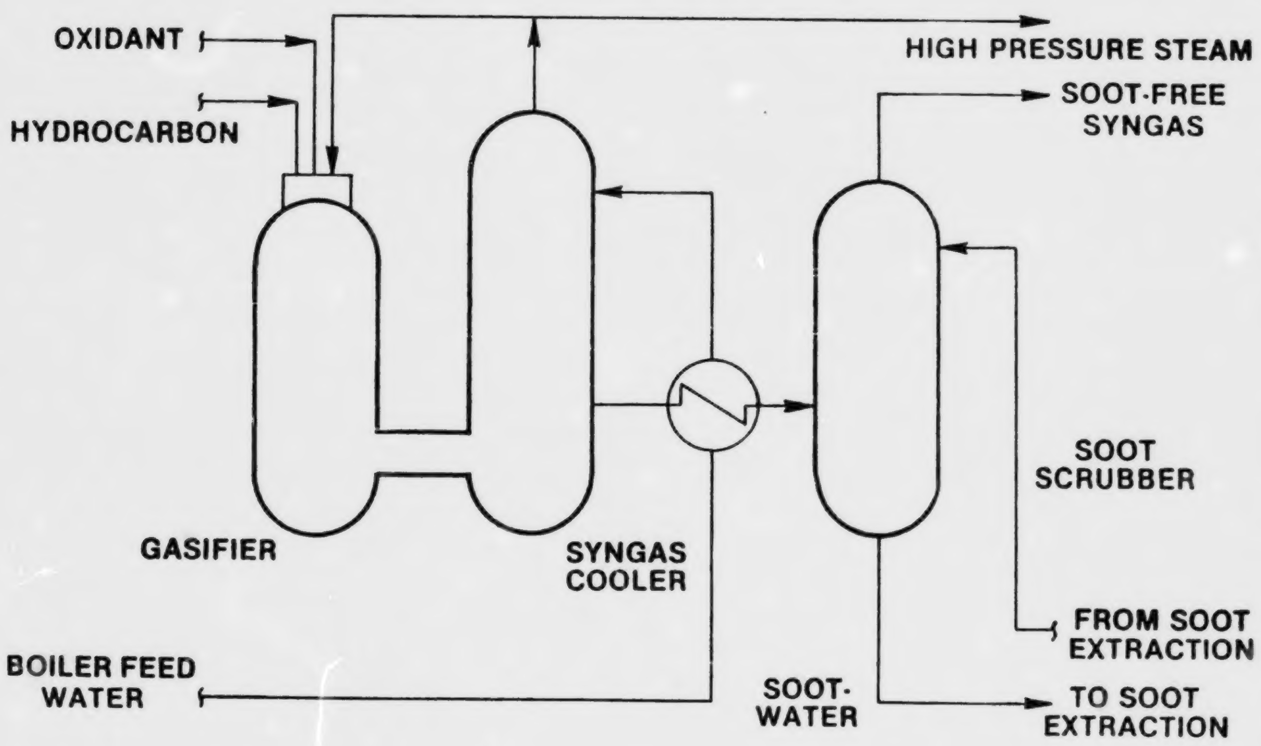
The three main licensors of non-catalytic gasification processes are Texaco, Shell and Koppers-Totzek. The first two operate at elevated pressure and the last near atmospheric pressure. Useful capital cost and utility consumption data have not been published because of the wide range of pitch feeds available and wide variation in product gas processing which depends on the ultimate use for the gas. As a result these values are not reported for the processes discussed below.

(a) Texaco

The Texaco gasification process was developed in 1946 to convert surplus natural gas to synthesis gas. The process has since been modified to gasify heavier feeds extending to heavy pitch and coal. A schematic flowsheet of the process is in Figure 3.26 (144). The pitch is fed to the gasifier as either a high temperature liquid, up to 260°C with heavy pitch, or as a wet ground solid pitch-water slurry in the case of very heavy pitch. The oil, steam and oxygen are fed to the process burner at the top of the reactor where effective mixing and combustion occur. The reactor is an open, uncooled, refractory lined, pressure vessel that operates at 1100-1600°C and at pressures up to 8.3 MPa (144). Texaco feels there are no technical obstacles to designing and operating the system for pressures up to 17.3 MPa (145). The liquid slag formed from ash in the feed drops into a water bath under the reactor and is removed through a lock vessel. The hot product gas from the reactor enters a waste heat boiler where the gas is cooled by generating high pressure steam first in a radiation cooler and then a convection cooler. For applications where the product gas is to be shift converted to reduce the CO content, the additional steam which must be added to the gas

FIGURE 3.26

TEXACO GASIFIER PROCESS FLOW SCHEMATIC


OXIDANT
HYDROCARBON
HIGH PRESSURE STEAM
SOOT-FREE SYNGAS
GASIFIER
SYNGAS COOLER
SOOT SCRUBBER
FROM SOOT EXTRACTION
BOILER FEED WATER
SOOT-WATER
TO SOOT EXTRACTION

is generated by cooling the reactor gas with a direct water quench. In both cases the cooled gas is scrubbed with water in a soot scrubber to remove the up to 3 mass percent of the feedstock that is converted to soot.

The water and soot stream is contacted with naphtha to transfer the soot to the naphtha phase. The two phases are separated in a decanter and the soot-free water is sent through a stripper for removal of hydrocarbon traces before being recycled to the soot scrubber. The naphtha-soot phase is mixed with some of the pitch feed and sent to a fractionator where the naphtha is recovered overhead with the soot staying with the bottoms pitch for recycle to the gasifier. With pitches that are too heavy for this process, the water and soot stream is clarified and the concentrated solids product can be recycled to the reactor.

Yields from the Texaco gasifier with different pitch feeds are in Table 3.31 (144). The data show that the CO/H_2 ratio in the product gas increases as the C/H ratio in the feed increases. After processing, the only by-products from the process will normally be CO_2, elemental sulphur, ash, and soot scrubber purge water.

Results have been published from pilot plant gasification of coal liquefaction pitch from the Ruhrkohle liquefaction plant in Germany (146). The Texaco gasifier operated successfully with the pitch fed as either a hot liquid or ground in a water slurry. The results are shown in Table 3.32 and are consistent with the data for the Illinois No. 6 coal residue in Table 3.31. The additional water added to the system with the solid pitch slurry results in an increase in the CO_2/CO ratio in the product gas and a resulting reduction in the cold gas efficiency. The gasifier operated at 3.6-4 MPa and 1150-1400°C during these tests.

Tests with Exxon Donor Solvent (EDS) pitch and SRC-I pitch have been done by the Electric Power Research Institute at Texaco's Montebello Research Laboratory. The EDS residue was fed as a water slurry from a wet grinding system. The gasifier produced 1.6-1.7 Nm^3 of $H_2 + CO$ per kg of pitch feed at cold gas efficiencies of 72-75% (147). The SRC-I pitch was fed as a hot liquid and produced about 2.2 Nm^3 of $H_2 + CO$ per kg of pitch feed at cold gas efficiencies of 80-85 percent. These results and those in Table 3.32 show a

TABLE 3.31

TEXACO GASIFIER YIELDS

		9.6° API Fuel Oil	9.6° API Fuel Oil	4.3° API VacResid	-14.6° API Asphalt	Illinois No. 6 Coal Residue	-11.4° API Coal Tar
(i)	Pitch Feed						
	Composition, mass percent						
	Carbon	87.2	87.2	83.80	85.94	69.73	88.1
	Hydrogen	9.9	9.9	9.65	9.49	5.21	5.7
	Nitrogen	0.7	0.7	0.31	1.40	0.81	0.9
	Sulphur	1.4	1.4	6.20	2.40	1.38	0.8
	Oxygen	0.8	0.8	-	0.47	2.70	4.4
	Chlorine	-	-	-	-	0.21	-
	Ash	-	-	0.04	0.3	19.96	0.1
	C/H Ratio, kg/kg	8.82	8.82	8.68	9.15	13.38	15.46
	Higher Heating Value, kJ/kg	42,320	42,320	40,300	38,160	30,230	36,490
(ii)	Feed Rates, per thousand normal cubic metres of dry product gas						
	Pitch, kg	340.9	329.8	346.1	357.8	466.2	375.7
	Steam, kg	156.8	186.9	173.1	103.2	186.4	196.6
	Oxygen, Nm^3	240	241	245	272	262	241
	Carbon, kg	10.8	(17.5)(a)	(5.8)(a)	(6.5)(a)	3.2	6.4
(iii)	Dry Product Gas, Nm^3/kg pitch feed	2.9	3.0	2.9	2.8	2.1	2.7
	Product Gas Composition, volume percent						
	Carbon monoxide	48.5	47.5	48.29	50.70	53.24	54.3
	Hydrogen	45.9	45.8	44.23	42.90	39.14	38.9
	Carbon dioxide	4.6	5.7	5.20	5.36	6.77	5.7
	Methane	0.2	0.5	0.57	0.10	0.01	0.1
	Argon plus nitrogen	0.7	0.2	0.21	0.45	0.32	0.8
	Hydrogen sulphide	0.1	0.3	1.42	0.49	0.49	0.2
	Carbonyl sulphide	0.0	0.0	0.08	0.00	0.03	0.0
(iv)	Performance Data						
	Specific Oxygen Consumption Nm^3/MNm^3 (H_2 + CO)	254	258	265	291	284	259
	H_2 + CO Gas Production Nm^3/kg pitch feed	2.8	2.8	2.7	2.6	2.0	2.5
	Cold Gas Efficiency, HHV of (H_2+CO) as percent of Hydrocarbon Higher Heating Value	83.1	84.7	84.1	82.2	83.1	86.4

Notes: (a) Recycled to extinction.

TABLE 3.32

TEXACO GASIFIER YIELDS FROM COAL LIQUEFACTION PITCH

	Solid Residue	Molten Residue
Carbon Conversion, percent	> 98	> 99
Syngas Production, Nm^3/t (mf)	1520	2000 (Approx.)
Cold Gas Efficiency, percent	78	82
Gas Composition, volume percent		
CO	45	58
H_2	36	35
CO_2	18	5
CH_4	< 0.1	0.3
Ratio CO/H_2	1.25	1.66

thermal efficiency advantage when the gasifier can be fed with molten pitch.

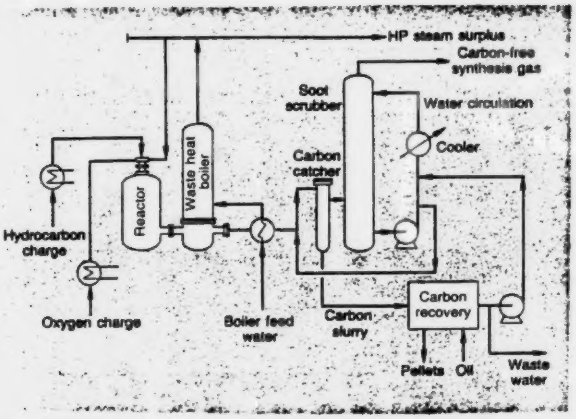
(b) Shell

The Shell gasification process is very similar in concept to the Texaco process discussed above. A schematic flowsheet is shown in Figure 3.27 (148). The gasification process takes place in an empty, refractory lined pressure vessel. The pitch feed is partially oxidized with oxygen (enriched or air) at pressures up to 6 MPa and steam is added to moderate the reaction temperature to 1400-1500°C. Any pitch that has a low enough viscosity at preheat temperature to be atomized effectively can be used in the process. This may require a fired preheater with heavy pitches rather than a steam heated preheater. With pitch feeds, up to 3 mass percent of the feed is converted to soot that is carried from the reactor with the product gas. The product gas is cooled to about 200°C in a waste heat boiler and economizer downstream of the reactor where steam is generated at 4-12 MPa. About 25-30 percent of the high pressure steam is used within the process with the balance available for export. To prevent carbon lay down in the exchanger tubing, helical coils and high gas velocities are used which have given reliable operation. The soot is removed from the cooled product gas in a two stage water wash to less than 1 mg/kg.

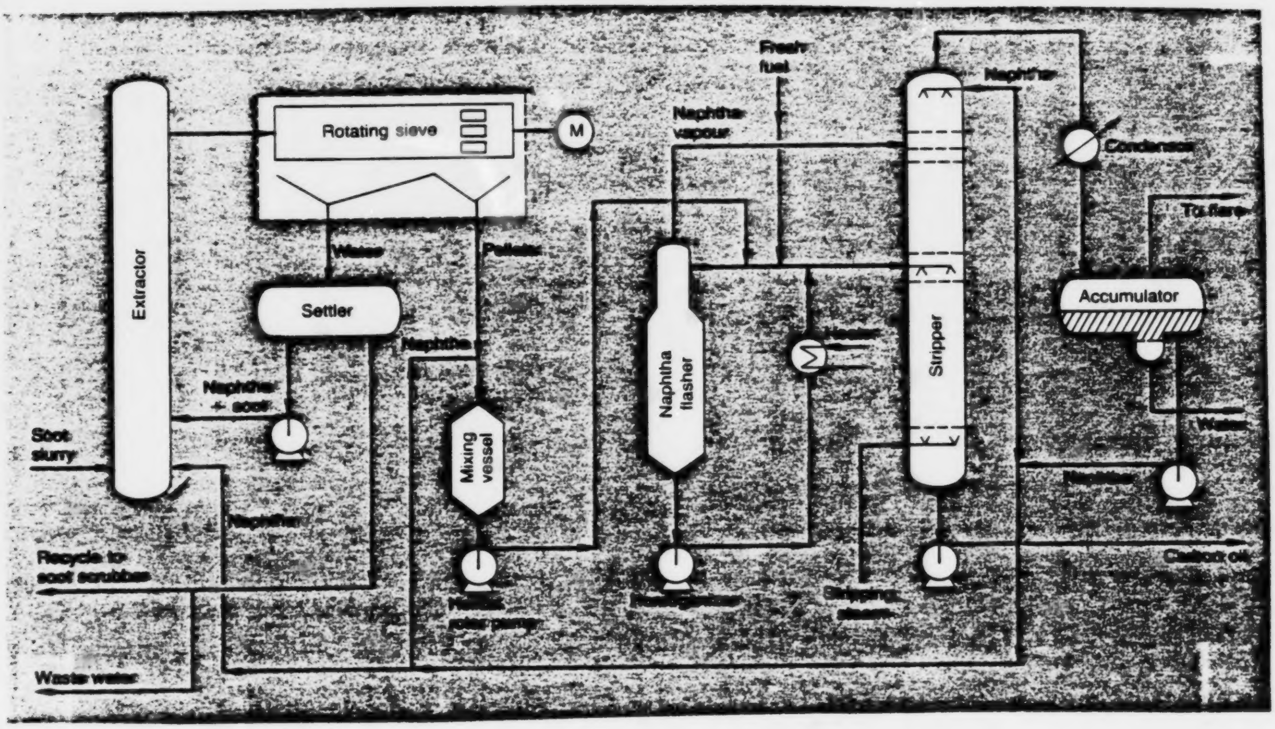
The soot is recovered from the wash water in the naphtha soot recovery unit (NSRU) shown in Figure 3.27. This system was developed as the gasifier process was used with heavy pitch feeds. The soot slurry is mixed with naphtha and the soot is agglomerated in a continuously stirred extractor. The soot is bound with naphtha in the agglomerated pellets. The extractor overflows to a rotating sieve where the bulk of the water is removed with the pellets being conveyed to the top of the sieve for removal. The pellets are mixed with extra naphtha and pumped to the naphtha flasher feed where mixing with hot pitch occurs. The pellets are shattered and dispersed in the pitch due to the rapid vapourization of the naphtha. The carbon oil from the bottom of the flasher is homogenized and heated with part recycled to the naphtha flasher and the balance sent to a column where the residual naphtha is recovered by steam stripping. The carbon oil is then recycled to the gasifier. The ash in the pitch feed is mostly removed in the waste water purge so that there is only a limited

FIGURE 3.27

SHELL GASIFIER PROCESS FLOW SCHEMATIC


HP steam surplus
Carbon-free synthesis gas
Soot scrubber
Water circulation
Cooler
Carbon catcher
Reactor
Waste heat boiler
Hydrocarbon charge
Oxygen charge
Boiler feed water
Carbon slurry
Carbon recovery
Pellets
Oil
Waste water

Gasifier Process


Extractor
Rotating sieve
M
Water
Pellets
Settler
Naphtha
Naphtha + soot
Soot slurry
Mixing vessel
Naphtha
Recycle to soot scrubber
Waste water
Fresh fuel
Naphtha vapour
Naphtha flasher
Stripper
Naphtha
Condenser
To flare
Accumulator
Water
Stripping steam
Carbon oil

Naphtha Soot Recovery Unit

buildup of ash in the system with complete soot recycle (23, 148).

Process yields for the production of 1000 Nm^3 of H_2 + CO are shown in Table 3.33 (149). The gas compositions are very similar to those from the Texaco gasifier shown in Table 3.31.

(c) Koppers-Totzek

The Koppers-Totzek (K-T) gasifier is well proven in commercial operation. Its main difference from the Texaco and Shell gasifiers is that it operates at just above atmospheric pressure. This can be a disadvantage if the synthesis gas product is to be subsequently processed at high pressure. A version of the process for pressurized operation at 3.0 MPa, called the PRENFLO process, is now being developed. The process is licensed by Krupp-Koppers and GKT Gesellschaft fur Kohle-Technologie.

A schematic of the K-T gasifier is in Figure 3.28 (150) showing the refractory lined, steam jacketed reactor vessel. The K-T gasifiers can be four-headed with the burners 90° apart or two-headed with the burners 180° apart firing horizontally. The reaction products leave the reactor at 1400-1600°C. Molten ash slag is fused by contact with water in a quench tank below the gasifier. The product gas is sprayed with water if necessary to freeze any entrained slag drops before entering the waste heat boiler. High pressure steam is generated in the waste heat boiler and economizer. The gas then goes to a spray tower where it is cooled to about 40°C and entrained particulates are removed by direct contact with spray water (150-152).

Product yields from pitch feeds have not been published recently. The product gas composition should be similar to the Texaco and Shell values since they are determined primarily by the equilibrium relations at these high reaction temperatures. These were found to be relatively insensitive to pressure in Section 3.4.1.

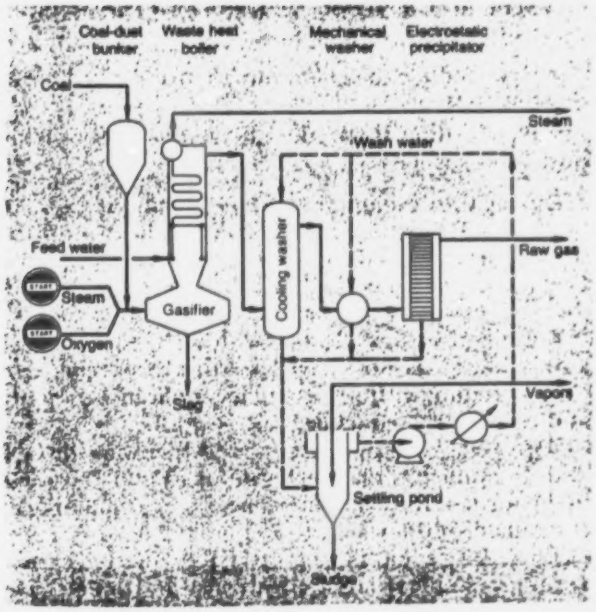
TABLE 3.33

SHELL GASIFIER YIELDS

	14.2°API Fuel Oil	14.2°API Fuel Oil	4.6°API Vac Resid	4.6°API Vac Resid	-1.1°API Asphalt
(i) Pitch Feed					
C/H Ratio, kg/kg	7.49	7.49	8.87	8.87	9.34
S, mass percent	3.50	3.50	4.50	4.50	4.92
Ash, mass percent	0.07	0.07	0.05	0.05	0.05
(ii) Feed Rates, per thousand normal cubic metres of H_2 + CO					
Pitch, kg	327.3	339.2	336.5	346.3	349.0
Steam, kg	136.0	277.8	167.1	247.9	172.9
Oxygen, Nm^3	245.9	271.8	240.4	261.2	243.8
(iii) Product Gas Composition, Volume percent					
Carbon monoxide	48.14	43.18	49.52	46.45	50.09
Hydrogen	46.74	47.34	44.80	44.95	43.69
Carbon dioxide	3.80	8.16	4.16	7.08	4.45
Methane	0.30	0.30	0.30	0.30	0.30
Argon plus nitrogen	0.23	0.30	0.18	0.18	0.30
Hydrogen sulphide	0.76	0.75	1.00	1.00	1.12
Carbonyl sulphide	0.03	0.03	0.04	0.04	0.05
Net product steam, kg per thousand Nm^3 H_2 + CO	695.1	792.2	631.6	735.6	666.6

FIGURE 3.28

KOPPERS-TOTZEK GASIFIER PROCESS FLOW SCHEMATIC


Coal-dust bunker
Waste heat boiler
Mechanical washer
Electrostatic precipitator
Coal
Steam
Wash water
Feed water
Raw gas
START
Steam
START
Oxygen
Gasifier
Cooling washer
Slag
Vapors
Settling pond
Sludge

(d) Hybrid Gasification and Dynacracking Processes

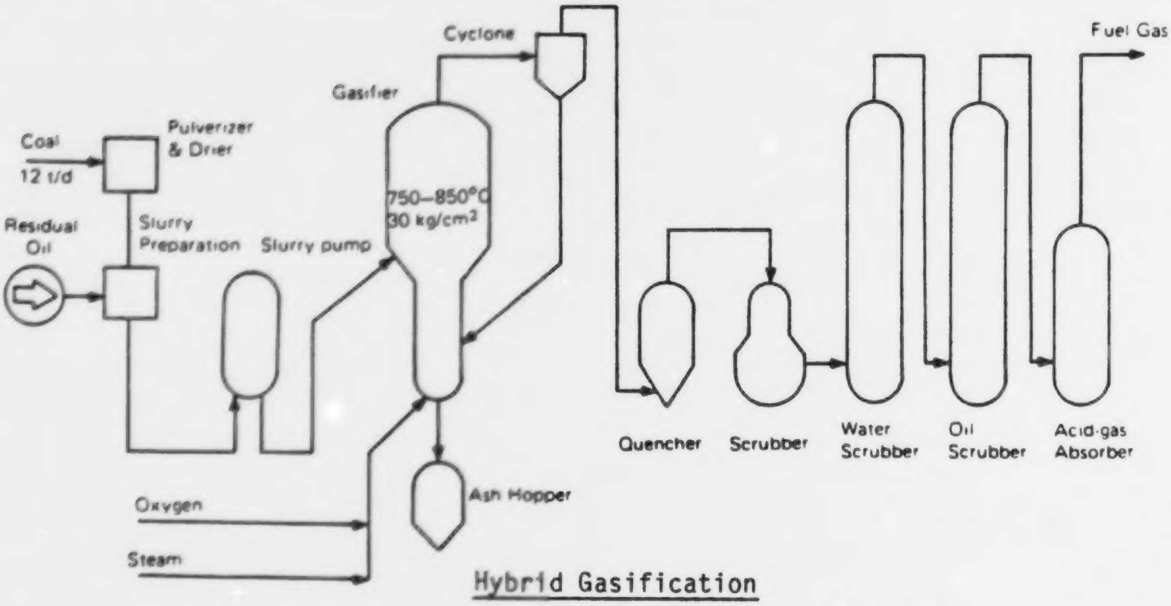
These processes are still under development but are discussed in this report because they are similar in process concept to the pyrolysis/gasification process that CANMET is proposing to develop. The Hybrid Gasification process is being developed in Japan for a slurry of coal in residual oil but should be able to feed pitch as well. The Dynacracking process is being developed by Hydrocarbon Research Inc. in the United States.

A schematic flowsheet of the Hybrid Gasification process is in Figure 3.29 (23). The process has a single fluidized bed where the pitch feed is gasified in two stages. The feed is thermally cracked in the upper reactor section at 750-850°C and 3 MPa producing gas, tar and char. The char is then gasified by oxygen and steam in the lower zone of the gasifier. Ash is quenched and discharged from the ash hopper. The product gas is quenched to about 450°C in a fluidized bed heat exchanger and then scrubbed to remove tar, dust and steam at about 200°C (23).

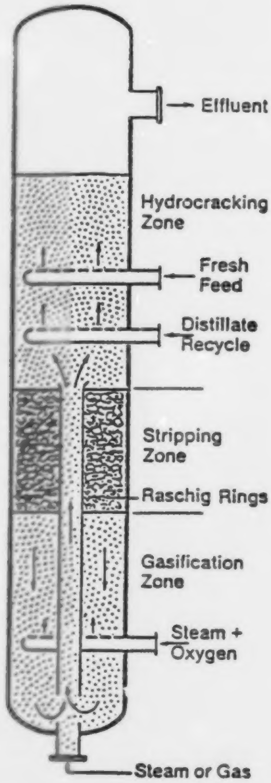
The Dynacracking process reactor is shown in Figure 3.29 (153). The reactor operates with a non-catalytic, moving bed of inert carrier. Pitch feed is converted to lighter products in the presence of the inert carrier and a hydrogen rich gas at about 540°C in the upper bed. Coke deposits on the carrier as the pyrolysis occurs. The carrier continuously moves down into the lower reactor zone where the coke is gasified by oxygen and steam at about 1000°C. A pressure of 2.9 MPa has been found desirable for maximum liquids production. Increasing the pyrolysis temperature above 540°C gives the process wide flexibility to increase the product yield from primarily naphtha and distillate liquids to light gases (153).

FIGURE 3.29

HYBRID GASIFICATION AND DYNACRACKING PROCESS FLOW SCHEMATICS


Cyclone
Fuel Gas
Gasifier
Coal
12 t/d
Pulverizer & Drier
750–850°C
30 kg/cm²
Residual Oil
Slurry Preparation
Slurry pump
Quencher
Scrubber
Water Scrubber
Oil Scrubber
Acid-gas Absorber
Ash Hopper
Oxygen
Steam

Hybrid Gasification


Effluent
Hydrocracking Zone
Fresh Feed
Distillate Recycle
Stripping Zone
Raschig Rings
Gasification Zone
Steam + Oxygen
Steam or Gas

Dynacracking

3.4.2 Catalytic Gasification

Catalytic gasification, or reforming, with steam is the predominant route for production of carbon monoxide and hydrogen from lighter hydrocarbons in the natural gas to naphtha range. The overall process can be represented by:

$$RH + aH_2O \longrightarrow bCH_4 + cCO + dCO_2 + eH_2$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Supported nickel has been the most cost effective catalyst. Carbon formation in the catalyst is a problem which increases with the molecular weight of the hydrocarbon feed. Continuous steam reforming of naphtha was made possible by modifying the catalyst to promote carbon gasification and to minimize reactions leading to carbon. With heavier feedstocks continuous operation is not possible and a more robust catalyst than nickel would be advantageous. Research in this area has concentrated on the use of alkali metal based catalysts (52).

Several research studies of catalytic pitch gasification are discussed below. In all cases with pitch, the pitch was first pyrolyzed in an inert atmosphere to remove the volatile reaction components and leave a residual char. The steam gasification of the char was then investigated. Catalyst cost and recovery will be a prime factor in catalyst selection but that has not been considered in these studies since their main purpose has been to evaluate catalysts and understand the catalytic gasification reaction.

Ono et al (154) studied the gasification of coal chars impregnated with nickel catalyst. Nickel nitrate was used and subsequently reduced to metallic nickel. The gasification was done with hydrogen at 850°C and 1.0 MPa. They found that catalytic gasification increased the size of the large pores in the char and created additional large diameter pores while non-catalytic gasification primarily enlarged pores smaller than 6 nm diameter. The addition of calcium to the nickel enhanced the hydrogasification rate.

The steam gasification of pitch without separate pyrolysis was studied by Kikuchi et al (155) at 900°C and 0.1 MPa in a fluidized bed using catalysts of alkali metal compounds on alumina support. They found that the catalytic activity increased with decreasing ionization potential of the alkali metals so that Cs> K> Na> Li. The gasification proceeded by carbon intermediates and the effect of the anions of the alkali metal compounds was minor except for chloride. They proposed a mechanism for the pitch gasification that had been suggested from earlier work on graphite- or carbon-steam reaction that is based on an oxygen transfer mechanism. The initial reaction is the reduction of the alkali salt to alkali metal or metal oxide

$$M_2CO_3 + 2C \longrightarrow 2M + 3CO$$

$$M_2CO_3 + C \longrightarrow M_2O + 2CO$$

The metal then reacts with steam to form hydroxide and hydrogen.

$$2M + 2H_2O \longrightarrow 2MOH + H_2$$

Alkali carbonate is then regenerated by reaction of the hydroxide with CO or CO_2.

$$2MOH + CO(CO_2) \longrightarrow M_2CO_3 + H_2(H_2O)$$

By assuming the formation of electron donor-acceptor complexes between deposited carbon and alkali metals they were able to explain the difference in alkali metal catalytic activity.

Sekhar and Ternan (156) studied the gasification of hydrocracked pitch char using potassium carbonate or vanadium pentoxide catalysts at 700 - 1200°C with steam. Compared to non-catalytic gasification, they found that the use of potassium carbonate enhanced the reaction rate while the vanadium pentoxide inhibited the rate. They questioned the validity of models such as proposed by Kikuchi et al (155) since their work showed that potassium carbonate did not exist as such under reaction conditions. Sekhar and Ternan explained the catalytic effect by potassium donating its outer electron to the π-electron clouds associated with the carbon layers. The extra electrons facilitate the formation of an unstable reaction intermediate which leads to CO. The vacant d-orbitals in vanadium, on the other hand, stabilize the

π-electron clouds in the carbon making CO evolution more difficult.

Further work was done by Ternan and Sekhar (157) with hydrocracked pitch char gasification using steam at 900°C with potassium carbonate catalyst. The gasification rate was proportional to the amount of char present indicating it is a first order reaction. They found that hydrogen formed almost instantaneously when steam reacted with the char but that some carbon-oxygen species remained adsorbed on the char surface. The formation of the carbon-oxygen bonds proceeded in the following sequence to carbon monoxide:

$$-C-OH \text{ (hydroxyl)} \longrightarrow -C{=}O \text{ (carbonyl)} \longrightarrow C{\equiv}O \text{ (carbon monoxide)}$$

The catalytic gasification processes discussed below are not commercially proven but they are included because they are similar in concept to the catalytic gasification process that CANMET is proposing to develop.

(a) M-Gas

The M-Gas process has been under development by Mitsui Engineering Co. in Japan since 1978 (158). Experimental work has gone as far as laboratory bench scale tests at a pitch feed rate of 4.5 kg/h. The process uses a fluidized bed of alkali metal catalyst for the carbon-steam gasification reaction with the heat of reaction provided by combustion of coke deposited on the catalyst. The reactor operates at about 900°C and just slightly above atmospheric pressure.

Pitch is fed to the middle section of the reactor where pyrolysis reactions initially take place resulting in methane, ethane and ethylene in the product gas and coke on the catalyst. Steam and oxygen are introduced through a perforated distributor at the bottom of the reactor where they react with the coke on the catalyst producing carbon oxides and hydrogen. The use of catalyst about doubled the yield of acid gas free product gas compared to operation with a sand bed at the same conditions. The catalyst, therefore, acts as a carrier for both coke and heat, and enhances the steam gasification reaction rate.

(b) Exxon Catalytic Gasification

Exxon Research and Engineering has been devloping a catalytic gasification process with a 1 t/d of coal development unit operating since 1979 (151). Potassium is used as the catalyst.

Crushed coal (or char) has an aqueous solution of potassium catalyst added and is fed to the fluidized bed reactor which operates at about 700°C and 3.4 MPa. Gasification, shift and methanation reactions all occur in the fluidized bed reactor to produce a high methane content product gas. The potassium catalyzes the gasification reactions allowing operation at the relatively low temperature of 700°C and the potassium-char then catalyzes the shift and methanation reactions with the result that gas phase equilibrium is attained. The lower reaction temperature favours methane production. The product gas is cooled to remove steam and scrubbed for acid gas (H_2S and CO_2) removal. The methane product is cryogenically separated from CO and H_2 which are recycled to the fluidized bed. The endothermic heat of gasification is about balanced by the exothermic heats of shift and methanation so that no oxygen is added to the reactor. The reactor heat requirement is provided by preheating the steam and CO-H_2 recycle gas to about 840°C for feed to the fluidized bed. Char containing catalyst, unreacted carbon and ash is continuously removed from the reactor. About 70 percent of the catalyst is recovered by water washing and is recycled to the catalyst addition where about 12 kg of KOH equivalent are added per 100 kg of dry feed coal.

(c) Tosco Process

A fluidized bed gasification process using alkali metal catalyst has been under development by Tosco Corp. since 1977 (159). Raw coal is mixed with the catalyst and fed to the reactor which operates at 650 - 815°C. The reactor is fluidized by superheated steam and oxygen which are fed to the bottom of the bed. The catalyst is not deactivated in the reaction and the makeup requirement of about 0.5 mass percent of coal feed is for the catalyst lost with the reactor fines. The gas produced from coke is about 45 volume percent H_2, 27 volume percent CO, 25 volume percent CO_2 with the balance methane and hydrogen sulphide. Advantages claimed for the process include: lower temperature operation allowing more carbon-steam reaction than non-catalytic processes, about half the oxygen requirement of a Texaco gasifier for the same

CO + H_2 yield, high carbon conversion, simpler mechanical design at the lower temperature, and reduced grinding costs with the coarse (6 mm) feed particles.

3.5 Pitch as a Coke and Electrode Binder

Non-coking coals can be used for the production of metallurgical grade coke by the addition of pitch (160). The non-coking coals have low fluidity, a low volatile content and are rich in inert macerals. The pitch acts as a fluidity enhancing agent, and by interacting with the vitrinite in the coal, it augments the supply of reactive carbon necessary for bonding together the inert macerals. Pitch from the commercial Eureka process unit in Japan has mainly been utilized as a coke binder in steel production (28).

CANMET did tests using pitch derived from hydrocracking Athabasca bitumen at four different conversion levels (160). The coal used was a western Canadian, low fluid, high rank bituminious coal with a relatively high concentration of inert macerals.

They found that the coke quality was a complex function of the amount of pitch added, the physico-chemical properties of the pitch and the fluidity of the coal/pitch blend. The blend had to be fluid enough to ensure a uniform and continuous distribution of binding material throughout the coal to ensure the incert macerals were adequately wetted to bond together. At a given pitch concentration in the blend, the fluidity increased for pitches obtained from higher severity hydrocracking. Since pitch aromaticity increases with the cracking severity, they suggested that the aromatics interact with the vitrinite so that the fluidity increased as the aromatics content increased.

The optimum coke strength was obtained when pitch was added in sufficient amount to generate a controlled fluidity with enough binding material to agglomerate the coke. If too much pitch was added, it had deleterious effects on the resultant coke which was not well understood but may be related to the development of micro-cracks within the coke matrix. The pitch content for maximum coke strength decreased as the Conradson carbon content of the pitch increased.

The electrode industries have primarily used coal tar pitches as binders. These pitches are highly aromatic with a high C/H ratio with negligible aliphatic carbon and low sulphur contents. They have a high softening point, low ash and a high coking value. The pitch acts as a thermoplastic binder holding the ground coke particles until baking or coking take place. The optimum pitch content for Soderberg electrodes is about 20 percent while a lower content is desired for prebaked electrodes. The quinoline insolubles fraction of the pitch (highly condensed aromatic compounds with as many as 20 - 25 rings) has an important influence on the coke formation from the pitch between the grains of ground coke. The quinoline insolubles contribute to the strength of the electrode by providing a strong bond between coke particles and lower the electrical resistivity. Petroleum pitches have been used more recently as electrode binders but their properties are not as favourable for electrode manufacture as coal tar pitches (161).

Imperial Oil evaluated coal tar and petroleum pitches as binders for both prebaked and Soderberg electrodes (162, 163). The petroleum pitch was the residue from fluid catalytic cracking. In both cases different carbon blacks were added to the petroleum pitch binder. The high surface area, small particle size reinforcing blacks improved the homogeneity and mechanical stability of the binder-coke electrode mixture by preventing the separation of oily components at high temperature and had a catalytic effect on polymerization and condensation reactions associated with coking of the binder. About 5 mass percent carbon black in pitch showed the best performance. Prebaked electrodes were made from ground coke with 20 - 25 mass percent binder added while the Soderberg electrode used 25 - 35 mass percent binder. In both cases the performance of the petroleum pitch based binder and resulting electrodes was similar to that with coal tar pitch. They also showed that addition of 2.5 mass percent carbon black to a coal tar with a low coking value and low quinoline insolubles content resulted in a marked improvement in performance as a Soderberg electrode binder.

P.R. #9041.14
File #9041.2

SECTION 4.0 - PHYSICAL AND CHEMICAL PROPERTIES OF PITCH

4.0 PHYSICAL AND CHEMICAL PROPERTIES OF PITCH

This section presents the results of a literature search to define the physical and chemical properties of pitch from a wide range of feedstocks and processes. The feedstock origins are conventional crude oils, heavy oils such as Lloydminster, bitumen, coal, and oil shale. Processes producing pitch that have been reviewed are vacuum distillation, catalytic cracking, residuum hydrodesulphurization, residuum hydrocracking, Eureka, Gulf Donor Refined Bitumen, solvent deasphalting, coal liquefaction, shale oil, and olefin pyrolysis.

The pitch properties are presented in tabular form in the accompanying Tables 4.1 to 4.12 as follows:

Table 4.1	Conventional Crude Oil
Table 4.2	Heavy Oil and Bitumen
Table 4.3	Residuum Hydrodesulphurization
Table 4.4	Residuum Hydrocracking
Table 4.5	Eureka Process
Table 4.6	Donor Refined Bitumen Process
Table 4.7	Solvent Deasphalting
Table 4.8	Fluid Catalytic Cracking
Table 4.9	Coal Liquefaction and Coal Tar
Table 4.10	Shale Oil
Table 4.11	Retorting
Table 4.12	Olefin Pyrolysis

The pitch properties given in the tables are primarily those that were defined by CANMET as of most interest and are:

(i) Proximate analysis - moisture, ash, volatile matter and fixed carbon.

(ii) Ultimate analysis - carbon, hydrogen, sulphur, nitrogen, oxygen and ash.

(iii) Ash Analysis - SiO_2, Al_2O_3, Fe_2O_3, Mn_3O_4, TiO_2, P_2O_5, CaO, MgO, SO_3, Na_2O, K_2O, V_2O_5 and NiO.

(iv) Boiling point, melting point and softening point.

(v) Specific gravity.

(vi) Viscosity and molecular weight.

(vii) Aromatic carbon and aromatic hydrogen.

(viii) Heptane-insoluble, pentane-insoluble, benzene-insoluble, and tetrahydrofuran-insoluble.

(ix) Conradson carbon residue.

(x) Heating value.

Most of the available analyses do not have all these properties. The reported values are presented in Tables 4.1 to 4.12 while the remaining properties are left blank to indicate no measurement. The "Pitch Source" defines the oil fraction in Tables 4.1, 4.2, 4.9 and 4.10 and the process feed stream in the remaining tables.

The pitch properties for the different feedstock sources and processes were obtained from a literature search and from direct contacts with process licensors. The literature search included the Applied Science and Technology Index, Engineering Index, Alberta Oil Sands Index, Alberta Coal Technology Index and an Asphaltene Bibliography prepared by the University of Calgary (3). The Asphaltene Bibliography was compiled from Chemical Abstracts. The literature review is comprehensive within the budget and scope of work for this part of the study but it is not intended to be all inclusive.

Since it was anticipated that all of the desired properties would not be available in published literature, direct contacts were made with thirteen process licensors requesting the required physical and chemical properties of pitch. The licensors contacted, processes for which data were requested, and the result of the contact are summarized in Table 4.13.

As much as possible, the properties given are for 525°C+ pitch but in some cases lower initial boiling point residuum fractions are given. Some whole heavy oil and bitumen properties are given in Table 4.2 since some of the process pitch residues shown in the subsequent tables are derived from these feedstocks. The work of Jacobs et al (192) should be referred to for more detailed trace metal concentrations in Athabasca, Cold Lake and Peace River whole bitumen, asphaltene and maltene fractions.

As shown in Table 4.3, the detailed properties of pitch from residuum hydrodesulphurization have not been widely published. Since the main purpose of this process has been the production of low sulphur fuel oil, the product properties usually published are sulphur content and specific gravity with nickel and vanadium contents in a few cases. It was felt that this was not sufficient to include in this report.

Boiling ranges were not given for the solvent deasphalting pitches in Table 4.7. The pitch streams shown are the asphaltene or residual stream from the process in all cases.

Pitch properties from fluid catalytic cracking and olefin pyrolysis in Tables 4.8 and 4.12, respectively, have not been widely reported. These streams are not usually 525°C+ and have a higher sales value than the pitches from most of the other processes. These feeds are, therefore, not prime candidates for the CANMET pyrolysis/gasification process.

Because of the nature of the retorting process for shale oil production and the Lurgi-Ruhrgas process, there is very little production of 525°C+ pitch (Tables 4.10 and 4.11). The potential heavy pitch remains in the pyrolysis section to be cracked to light products and coke. These processes are not likely to produce significant pitch feed for the CANMET pyrolysis/gasification process.

DESCRIPTION TABLE 4.1 CONVENTIONAL CRUDE OIL

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985
BY SD

JOB NO. 9041

Pitch Source	IPL #1 Vacuum Tower Bottoms	Canadian Blend Vac. Resid.	Bow River Heavy Vac. Resid.	Federated Light & Medium Vac. Resid.	Gulf Alberta Light & Medium Vac. Resid.	Rainbow Light & Medium Vac Resid.	Rangeland-S Light & Medium Vac. Resid.	West Texas Intermediate Vac. Resid.	Arabian Extra Light 535°C+	Arabian Light 535°C+	Arabian Light Vac. Resid.	Arabian Light Vac. Resid.	Arabian Medium 535°C+
Proximate Analysis, mass percent													
Moisture													
Ash													
Volatile matter													
Fixed Carbon													
Ultimate Analysis, mass percent													
C		86.98						86.90	85.61	85.79		85.02	83.86
H		11.37						11.42	11.30	10.65		10.17	9.91
S	0.92	1.37	3.82	0.54	2.39	1.07	1.22	1.13	2.95	4.16	4.0	4.34	5.31
N	0.49	0.45				3.22		0.42	0.15	0.29	0.44	0.26	0.24
O													
Ash		0.034									0.05	0.03	
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3	29 (1)	34 (1)						69 (1)	11 (1)	28 (1)	7 (1)	28 (1)	14 (1)
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													
MgO													
SO_3													
Na_2O								66 (1)			24 (1)		
K_2O													
V_2O_5	17 (1)	32 (1)	169 (1)	5.7 (1)	25 (1)	2.9 (1)	7 (1)	42 (1)	25.9 (1)	59 (1)	66 (1)	102 (1)	68 (1)
NiO	14 (1)	24 (1)	68 (1)	9.5 (1)	24 (1)	4.6 (1)	3 (1)	23 (1)	7.2 (1)	17 (1)	24 (1)	25 (1)	24 (1)
Boiling Point, °C	500°C+	90% 524°C+	565°C+	565°C+	565°C+	565°C+	565°C+	–	535°C+	535°C+	538°C+	552°C+	535°C+
Melting Point, °C													
Softening Point, °C	34		73 (Pour)	26 (Pour)	44 (Pour)	28 (Pour)	28 (Pour)	38	24 (Pour)	41 (Pour)	27 (Pour)		42 (Pour)
Specific Gravity/°API	0.985/12.1	0.989/11.6	1.034/5.3	0.965/15.2	0.969/14.6	0.936/19.6	0.924/21.7	0.990/11.5	0.987/11.9	1.011/8.5	1.017/8.5	1.019/7.4	1.028/6.15
Molecular Weight								1037			855		
Viscosity mm^2/s @ °C	116 @ 135		940@135	31 @ 135	60@135	28@135	19@135	610@99	181@99	799@99	37,000@54	3660@82	1600@99
mm^2/s @ °C								68@149			850@99	1070@99	
Aromatic Carbon, mass percent													
Aromatic Hydrogen, mass percent											3.7 of H		
Insolubles in, mass percent													
Heptane								2.79					
Pentane		11.8						6.35				13.55	
Benzene													
Tetrahydrofuran													
Conradson Carbon Residue, mass%	18.4	15.9				11.1		15.6	10.7	15.2	14.5	22.3	19.8
Heating Value, kJ/kg													
Reference Number	141	122	164	164	164	164	164	12	165	165	166	132	165

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.1 CONVENTIONAL CRUDE OIL (Cont'd)

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985

BY SD

JOB NO. 9041

CDOA 11 11-84

Pitch Source	Arabian Heavy 343°C+	Arabian Heavy 535°C+	Arabian Heavy Vac. Resid	Iranian Light Vac Resid	Iranian Heavy Vac Resid
Proximate Analysis, mass percent					
Moisture					
Ash					
Volatile matter					
Fixed Carbon					
Ultimate Analysis, mass percent					
C	84.41	83.37			
H	10.95	9.90			
S	4.35	5.2	5.6	3.3	3.4
N	0.29	0.37	0.67	0.54	0.68
O					
Ash			0.03		
Ash Analysis, mass percent					
SiO_2					
Al_2O_3					
Fe_2O_3		33 (1)	10 (1)	< 2.4 (1)	62 (1)
Mn_3O_4					
TiO_2					
P_2O_5					
CaO					
MgO					
SO_3					
Na_2O			1 (1)		
K_2O					
V_2O_5	85 (1)	148 (1)	160 (1)	190 (1)	400 (1)
NiO	27 (1)	46 (1)	60 (1)	68 (1)	115 (1)
Boiling Point, °C	343°C+	535°C+	538°C+	538°C+	538°C+
Melting Point, °C					
Softening Point, °C		42 (Pour)	57 (Pour)	32 (Pour)	65 (Pour)
Specific Gravity/°API	0.984/12.3	1.032/5.6	1.040/4.6	1.014/8.0	1.025/6.6
Molecular Weight			940		
Viscosity mm^2/s @ °C		520 @ 135	7000 @ 99	1200 @ 99	2490 @ 99
mm^2/s @ °C					
Aromatic Carbon, mass percent					
Aromatic Hydrogen, mass percent				3.6 of H	
Insolubles in, mass percent					
Heptane					
Pentane					
Benzene					
Tetrahydrofuran					
Conradson Carbon Residue, mass%		22.4	23.5	18.5	20.0
Heating Value, kJ/kg					
Reference Number	94	165	166	166	166

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.2 HEAVY OIL AND BITUMEN
CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES
DATE December, 1985
BY SD
JOB NO. 9041

Pitch Source	Canadian Heavy Oil Vac Resid	Whole Lloydminster Heavy Oil	Lloydminster Heavy Oil 343°C+	Lloydminster Heavy Oil 343°C+	Whole Cold Lake Bitumen	Cold Lake Bitumen Vac. Resid.	Whole Athabasca Bitumen	Whole Athabasca Bitumen	Whole Athabasca Bitumen	Whole Athabasca Bitumen	Whole Athabasca Bitumen	Whole Athabasca Bitumen	Whole Athabasca Bitumen
Proximate Analysis, mass percent													
Moisture													
Ash													
Volatile matter													
Fixed Carbon													
Ultimate Analysis, mass percent													
C		82.8	83.72	84.28	83.95		83.26	80.0		82.9 - 83.6	82.5	83.15	83.12
H		11.8	10.69	10.70	10.46		10.43	10.0		10.3 - 10.6	10.3	10.29	10.59
S	7.3	3.44	4.6	4.41	4.70	5.82	4.61	5.7	4.30	4.2 - 5.5	4.86	4.57	4.75
N	0.52	0.27	0.36	0.38	0.23	0.56	0.44	0.6	0.37	0.3 - 0.6	0.47	0.4	0.4
O		1.69	0.72	0.04	0.95			3.7		0.2 - 1.3	1.7	1.6	1.14
Ash						0.11	0.45		0.42		0.02		
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3	16 (1)						190 (1)	620 (1)					75 (1)
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													26 (1)
MgO													47 (1)
SO_3													
Na_2O							12 (1)						20 (1)
K_2O													
V_2O_5	271 (1)		144 (1)	163 (1)		340 (1)	190 (1)	200 (1)	180 (1)		180 (1)		290 (1)
NiO	221 (1)		76 (1)	83 (1)		140 (1)	78 (1)	80 (1)	60 (1)		112 (1)		82 (1)
Boiling Point, °C	500°C+	–	343°C+	343°C+	–	500°C+	162°C+	–	–	–	–	–	–
Melting Point, °C													
Softening Point, °C	47												
Specific Gravity/°API	1.033 / 5.5	0.958/16.2	1.008/8.9	0.996/10.6		1.054/2.6	1.003/9.6		1.007/9.0	/6.5-8.6	0.989/11.6		1.013 / 8.2
Molecular Weight		380			490							540	539
Viscosity mm^2/s @ °C	610@ 135	380@38		169@ 99			3100@50						[illegible]
mm^2/s @ °C				67@ 121									[illegible]
Aromatic Carbon, mass percent													
Aromatic Hydrogen, mass percent													
Insolubles in, mass percent													
Heptane				10.1		15.8			8.3				
Pentane													
Benzene													
Tetrahydrofuran													
Conradson Carbon Residue, mass%	17.8			13.6 (RCR)		26.3	13.6	15.6	14.8		16.1 (RCR)		
Heating Value, kJ/kg											41,170		
Reference Number	141	167	94	168	169	88	136	96	88	170	171	169	167

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.2 HEAVY OIL AND BITUMEN (Cont'd)
CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES
DATE December, 1985
BY SD
JOB NO. 9041

Pitch Source	Athabasca Bitumen Vac. Resid.	Athabasca Bitumen Vac. Resid	Athabasca Bitumen Vac. Resid.	Athabasca Bitumen Vac. Resid.	Whole Tar Sand Triangle Bitumen	Whole Asphalt Ridge Bitumen	Whole Orinoco Crude	Orinoco Vac. Resid.					
Proximate Analysis, mass percent													
Moisture													
Ash													
Volatile matter													
Fixed Carbon													
Ultimate Analysis, mass percent													
C			82.8	83.2	84.0	85.2	84.84	84.10					
H			7.9	9.8	10.1	11.7	10.62	10.34					
S	5.72	6.9	5.8	6.3	4.38	0.59	4.09	4.05					
N	0.56	0.66	1.0	0.78	0.46	1.02	0.40	0.67					
O					1.1	1.1							
Ash	0.75		1.6		0.12	0.004		0.32					
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3		72 (1)		259 (1)				130 (1)					
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													
MgO													
SO_3													
Na_2O								58 (1)					
K_2O													
V_2O_5	310 (1)	370 (1)		378 (1)	108 (1)	25 (1)	417 (1)	457 (1)					
NiO	100 (1)	111 (1)		98 (1)	53 (1)	120 (1)	99 (1)	107 (1)					
Boiling Point, °C	500°C+	500°C+	525°C+	524°C+	–	–	–	–					
Melting Point, °C													
Softening Point, °C		70		75				32					
Specific Gravity/°API	1.060/2.0	1.061/1.9		1.076/0.0	0.992/11.1	0.970/14.4	1.009/8.6	1.020/7.3					
Molecular Weight			1300					778					
Viscosity mm^2/s @ °C		2214 @ 135		3850 @ 135									
mm^2/s @ °C				410 @ 177									
Aromatic Carbon, mass percent			47.8 of C										
Aromatic Hydrogen, mass percent			8.1 of H										
Insolubles in, mass percent													
Heptane	12.5												
Pentane			39.5										
Benzene													
Tetrahydrofuran													
Conradson Carbon Residue, mass%	25.0	23.2		22	21.6 (RCR)	3.5 (RCR)	13.4 (RCR)	16.4					
Heating Value, kJ/kg					41,635	43,730							
Reference Number	88	141	60	172	171	171	94	107					

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DEPARTMENT OF

DESCRIPTION TABLE 4.3 RESIDUUM HYDRODESULPHURIZATION CUSTOMER ENERGY, MINES AND RESOURCES

DATE December, 1985

BY SD

JOB NO. 9041

	Chevron RDS	Chevron RDS	Chevron VRDS	Chevron VRDS									
Pitch Source	Lloydminster	Arabian	Alaskan	Arabian									
	343°C+	Heavy 388°C+	454°C+	Light 538°C+									
	Feed	Feed	Feed	Feed									
Proximate Analysis, mass percent													
Moisture													
Ash													
Volatile matter													
Fixed Carbon													
Ultimate Analysis, mass percent													
C		86.9		88.3									
H	11.44	11.5		11.5									
S	0.55	1.1	0.4	0.46									
N	0.31	0.25	0.4	0.19									
O													
Ash													
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3		3 (1)		<3 (1)									
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													
MgO													
SO_3													
Na_2O													
K_2O													
V_2O_5	7 (1)	63 (1)	42 (1)	10 (1)									
NiO	9 (1)	24 (1)	21 (1)	5 (1)									
Boiling Point, °C	524°C+	510°C+	538°C+	538°C+									
Melting Point, °C													
Softening Point, °C													
Specific Gravity/°API	0.964/15.3	0.963/15.5	0.981/12.8	0.955/16.6									
Molecular Weight		860	910	846									
Viscosity mm^2/s @ °C		274@99		187@100									
mm^2/s @ °C													
Aromatic Carbon, mass percent													
Aromatic Hydrogen, mass percent													
Insolubles in, mass percent													
Heptane		8.5	6.5	2.8									
Pentane													
Benzene													
Tetrahydrofuran													
Conradson Carbon Residue, mass%	9.8 (RCR)	13.6 (RCR)	13.8 (RCR)	10.3 (RCR)									
Heating Value, kJ/kg													
Reference Number	168	168	168	168									

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

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DESCRIPTION TABLE 4.4 RESIDUUM HYDROCRACKING

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985

BY SD

JOB NO. 9041

	H-Oil 90% Conversion with vacuum bottoms recycle	H-Oil	H-Oil 85% Feed pitch conversion	H-Oil	H-Oil 95% Conversion with vacuum bottoms recycle	H-Oil	H-Oil 85% Feed pitch conversion	LC-Fining 55% Feed pitch conversion	LC-Fining	CANMET 80% Feed pitch conversion	CANMET Hydrocracking with additive 89 mass % conversion	CANMET Hydrocracking with additive 93 mass % conversion	CANMET Thermal Hydrocracking
Pitch Source	Lloydminster	Cold Lake	Cold Lake	Whole	Whole	Alaskan	Arabian	Lloydminster	Whole	IPL	Cold Lake	Cold Lake	Whole
	Atmospheric	331°C+	Atmospheric	Athabasca	Athabasca	482°C+	Heavy	Atmospheric	Athabasca	Resid	Vac. Resid.	Vac. Resid.	Athabasca
Proximate Analysis, mass percent	Resid. Feed	Feed	Resid. Feed	Bitumen Feed	Bitumen Feed	Feed	343°C+ Feed	Resid. Feed	Bitumen Feed	Feed	Feed	Feed	Bitumen Feed
Moisture													0
Ash									2.0				5.2
Volatile matter													42.4
Fixed Carbon													52.4
Ultimate Analysis, mass percent													
C		86.86	86.21	84.28		87.70	87.48		84.28	83.98	87.46	87.85	79.6
H	8.75	8.85	8.86	7.64		9.48	8.75		8.92	7.02	6.84	6.22	6.8
S	3.58	3.06	3.12	3.47	5.5	1.48	2.95	3.7	4.1	3.25	3.27	2.98	5.4
N	1.04	1.09	1.01	1.06	1.7	0.74	0.83		0.85	1.28			1.5
O		0.88	0.76						1.85				1.5
Ash		0.15		3.38						5.69			5.2
Ash Analysis, mass percent													
SiO_2													43.3
Al_2O_3													24.7
Fe_2O_3		92 (1)		18 (1)		7 (1)							11.4
Mn_3O_4													0.3
TiO_2													6.6
P_2O_5													0.3
CaO													2.8
MgO													1.6
SO_3													1.2
Na_2O													0.2
K_2O													1.7
V_2O_5		337 (1)	235 (1)	232 (1)		55 (1)	93 (1)			405 (1)			3.1
NiO		173 (1)	125 (1)	175 (1)		48 (1)	88 (1)			236 (1)			0.8
Boiling Point, °C	524°C+	525°C+	524°C+	525°C+	524°C+	525°C+	524°C+	524°C+	—	525°C+	524°C+	524°C+	525°C+
Melting Point, °C													
Softening Point, °C		89		92						119			
Specific Gravity/°API	1.093/-2.0	1.102/-3.1	1.098/-2.6	1.150/-8.5	1.160/-9.5	1.074/0.3	1.101/-3	1.047/3.7	1.084/-1.0	1.179/-11.5	1.23/-16.5	1.27/-20.1	
Molecular Weight										360			
Viscosity mm^2/s @ °C		379 @ 149		7930 @ 121		12,400 @ 99		206,000 @ 50					
mm^2/s @ °C		95 @ 177		165 @ 177		294 @ 149							
Aromatic Carbon, mass percent													67 of C
Aromatic Hydrogen, mass percent													
Insolubles in, mass percent													
Heptane										55.0			
Pentane		36.1		34.2		28.8					81.2	89.7	70.1 with ash
Benzene													27.1 with ash
Tetrahydrofuran													12.4 with ash
Conradson Carbon Residue, mass%		36.29 (RCR)	36.0 (RCR)	43.2 (RCR)		30.6 (RCR)	33.1	26.0		57.7 (RCR)	66.1	64.2	63.5
Heating Value, kJ/kg													
Reference Number	94	173	128	173	127	173	94	174	175	9	133	133	62

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.4 RESIDUUM HYDROCRACKING (Cont'd)   CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES   DATE December, 1985   BY SD   JOB NO. 9041

	CANMET Thermal Hydrocracking Low Severity	CANMET Thermal Hydrocracking High Severity	CANMET Thermal Hydrocracking	CANMET 76% Feed pitch conversion	CANMET Hydrocracking with additive 85 mass % conversion								
Pitch Source	Whole	Whole	Whole	Arabian	Arabian								
	Athabasca	Athabasca	Athabasca	Light Vac.	Light 552°C+								
	Bitumen Feed	Bitumen Feed	Bitumen Feed	Resid. Feed	Feed								
Proximate Analysis, mass percent													
Moisture													
Ash	1.8	5.8											
Volatile matter	73.1	44.6											
Fixed Carbon													
Ultimate Analysis, mass percent													
C	1.32 H/C	0.94 H/C	80.6	84.06	87.5								
H	atomic	atomic	6.6	7.54	6.5								
S	5.58	4.85	5.5	3.54	4.27								
N			1.2	1.20	0.78								
O													
Ash			5.1	0.95	0.68								
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3													
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													
MgO													
SO_3													
Na_2O													
K_2O													
V_2O_5				231 (1)									
NiO				156 (1)									
Boiling Point, °C	525°C+	525°C+	525°C+	525°C+	524°C+								
Melting Point, °C													
Softening Point, °C	50	135		102									
Specific Gravity/°API	1.10/-2.9	1.24/-17.4		1.144/-7.8	1.263/-19.5								
Molecular Weight			1000	400									
Viscosity mm^2/s @ °C													
mm^2/s @ °C													
Aromatic Carbon, mass percent			58.6 of C										
Aromatic Hydrogen, mass percent			15.6 of H										
Insolubles in, mass percent													
Heptane				33.7									
Pentane			73.5		78								
Benzene	2.6	20.6											
Tetrahydrofuran													
Conradson Carbon Residue, mass%	34.7	64.6		45.4(RCR)	63.5								
Heating Value, kJ/kg													
Reference Number	160	160	60	9	132								

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.5 EUREKA PROCESS

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985

BY SD

JOB NO. 9041

Pitch Source	Lloydminster Vac. Resid Feed	Whole Cold Lake Feed	Cold Lake Vac. Resid. Feed	Whole Athabasca Bitumen Feed	Athabasca Bitumen Vac Resid. Feed	Athabasca 520°C+ Vac. Resid. Feed							
Proximate Analysis, mass percent													
Moisture													
Ash													
Volatile matter	44.4	40.1	39.1	40.7	41.9	43.1							
Fixed Carbon						56.9							
Ultimate Analysis, mass percent													
C	82.8	84.9		82.5		82.1							
H	5.9	5.4		5.4		5.6							
S	4.6	6.5	6.6	6.6	6.6	66							
N	1.0	1.1		1.1		1.4							
O													
Ash	3.5	0.33	0.30	2.2	2.3	39							
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3													
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													
MgO													
SO_3													
Na_2O	8200 (1)	60 (1)		90 (1)									
K_2O													
V_2O_5	440 (1)	990 (1)		1090 (1)		1000 (1)							
NiO	210 (1)	370 (1)		410 (1)		350 (1)							
Boiling Point, °C	–	525°C+	525°C+	525°C+	525°C+	550°C+							
Melting Point, °C													
Softening Point, °C	230	260	200	250	200	185							
Specific Gravity/°API		1.26/-19.2		1.26/-19.2									
Molecular Weight													
Viscosity mm^2/s @ °C		3500@177		3100@177									
mm^2/s @ °C													
Aromatic Carbon, mass percent													
Aromatic Hydrogen, mass percent													
Insolubles in, mass percent													
Heptane	73.1	80.6		80.4		81.0							
Pentane													
Benzene	47.8	56.3		55.9		50.6							
Tetrahydrofuran													
Conradson Carbon Residue, mass%		77.0		75.7									
Heating Value, kJ/kg		36,600	36,700	35,700	35,700								
Reference Number	176	176	28	176	28	177							

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

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DESCRIPTION TABLE 4.6 DONOR REFINED BITUMEN PROCESS
CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES
DATE December, 1985
BY SD
JOB NO. 9041

Pitch Source	IPL #1 Vac. Resid Feed	Athabasca Bitumen Vac. Resid. Feed											
Proximate Analysis, mass percent													
Moisture													
Ash													
Volatile matter													
Fixed Carbon													
Ultimate Analysis, mass percent													
C													
H													
S	1.46	6.1											
N	1.03	1.26											
O													
Ash													
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3													
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													
MgO													
SO_3													
Na_2O													
K_2O													
V_2O_5	39.3 (1)	1225 (1)											
NiO	28.5 (1)	316 (1)											
Boiling Point, °C	504°C+	504°C+											
Melting Point, °C													
Softening Point, °C	89	100.6											
Specific Gravity/°API	1.205/-14.1	1.173/-10.9											
Molecular Weight													
Viscosity mm^2/s @ °C	1141 @ 150	5470 @ 150											
mm^2/s @ °C													
Aromatic Carbon, mass percent													
Aromatic Hydrogen, mass percent													
Insolubles in, mass percent													
Heptane													
Pentane													
Benzene													
Tetrahydrofuran													
Conradson Carbon Residue, mass%	52.3	47.7											
Heating Value, kJ/kg													
Reference Number	139	139											

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.7 SOLVENT DEASPHALTING

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985

BY SD

JOB NO. 9041

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	Demex Process	ROSE Process n-Pentane solvent	ROSE Process n-Butane solvent	ROSE Process n-Pentane solvent	ROSE Process n-Pentane solvent	ROSE Process n-Hexane solvent	ROSE Process n-Butane Solvent	ROSE Process n-Pentane solvent					
Pitch Source	West Texas	Typical	Cold Lake	Cold Lake	Whole	Whole	Arabian	Arabian					
	Intermediate	Petroleum	Reduced	Reduced	Athabasca	Athabasca	Light Vac.	Light Vac.					
	Vac. Resid	Pitches	Crude	Crude	Bitumen Feed	Bitumen Feed	Resid. Feed	Resid. Feed					
Proximate Analysis, mass percent													
Moisture		< 0.1											
Ash		0.1-0.4											
Volatile matter		70-75											
Fixed Carbon		25-30											
Ultimate Analysis, mass percent													
C	87.26	83-85											
H	9.29	8											
S	2.37	2-7	6.9	7.0	7.9	8.3	5.4	5.7					
N	0.86	0.5-2	0.94	1.02	1.03	1.06	0.58	0.66					
O													
Ash													
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3	373 (1)												
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													
MgO													
SO_3													
Na_2O	319 (1)												
K_2O													
V_2O_5	193 (1)	200-2000 (1)	580 (1)	885 (1)	345 (1)	530 (1)	214 (1)	290 (1)					
NiO	83 (1)	100-1000 (1)	235 (1)	350 (1)	115 (1)	200 (1)	65 (1)	87 (1)					
Boiling Point, °C	–	–	–	–	–	–	–	–					
Melting Point, °C													
Softening Point, °C	143	149-177	112	146	176	243	135	177					
Specific Gravity/°API	1.115/-4.6	1.13-1.15/	1.069/0.9	1.119/-5.0	1.193/-12.9	1.208/-14.4	1.110/-4.1	1.140/-7.4					
Molecular Weight	1814												
Viscosity mm^2/s @ °C	2987 @ 204	7000 @ 232	419,000 @ 135										
mm^2/s @ °C	216 @ 260	440 @ 288	99,000 @ 152										
Aromatic Carbon, mass percent													
Aromatic Hydrogen, mass percent													
Insolubles in, mass percent													
Heptane	19.8												
Pentane	44.1												
Benzene													
Tetrahydrofuran													
Conradson Carbon Residue, mass%	43.73	40-60	32	40	45	49	43	52					
Heating Value, kJ/kg		37,200-39,500											
Reference Number	12	178	178	178	178	178	13	13					

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.8 FLUID CATALYTIC CRACKING

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985
BY SD

JOB NO. 9041

	Kellogg HOC Decant Oil	Slurry Oil	Pitch
Pitch Source	North Sea 343°C+ Feed	Not Defined	Not Defined
Proximate Analysis, mass percent			
Moisture			
Ash			
Volatile matter			
Fixed Carbon			
Ultimate Analysis, mass percent			
C		88.4	94.8
H		8.4	4.6
S	1.40	0.9	
N			0.4
O			0.2
Ash	0.41		
Ash Analysis, mass percent			
SiO_2	3.7 (1)		
Al_2O_3			
Fe_2O_3	7.9 (1)		
Mn_3O_4			
TiO_2			
P_2O_5			
CaO			
MgO			
SO_3			
Na_2O	42 (1)		
K_2O			
V_2O_5	0 (1)		
NiO	2.2 (1)		
Boiling Point, °C	343°C+	–	270°C+
Melting Point, °C			
Softening Point, °C			
Specific Gravity/°API	1.108/-3.8	1.060/-2.0	
Molecular Weight			600
Viscosity mm^2/s @ °C	357 @ 50		
mm^2/s @ °C	15 @ 100		
Aromatic Carbon, mass percent			90 of C
Aromatic Hydrogen, mass percent			70 of H
Insolubles in, mass percent			
Heptane		1.0	
Pentane			
Benzene			38.3
Tetrahydrofuran			
Conradson Carbon Residue, mass%	6.82		
Heating Value, kJ/kg			
Reference Number	179	180	181

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.2 COAL LIQUEFACTION AND COAL TAR
CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES
DATE December, 1985
BY SD
JOB NO. 9041

	SRC-I	SRC-II	Exxon Donor Solvent	Exxon Donor Solvent	Exxon Donor Solvent	Exxon Donor Solvent	Exxon Donor Solvent	Exxon Donor Solvent	Exxon Donor Solvent	H-Coal	H-Coal	H-Coal	H-Coal
Pitch Source	Kentucky 9/14 coal liquefaction residue	Kentucky 9/14 coal liquefaction residue	Illinois No.6 coal liquefaction residue	Illinois No.6 coal liquefaction residue	Illinois No.6 coal liquefaction residue	Illinois No.6 coal liquefaction residue	Wyodak coal liquefaction residue	Wyodak coal liquefaction residue	Texas lignite liquefaction residue	Illinois No.6 coal liquefaction residue	Illinois No.6 coal liquefaction residue	Wyodak coal liquefaction residue	Wyodak coal liquefaction residue
Proximate Analysis, mass percent												(Period 21B)	(Period 35B)
Moisture	Trace				Dry	<1.0	Dry	<1.0	<1.0				
Ash					25.49	21.0	24.83	21.2	33.4				
Volatile matter					31.21	49.1	35.38	43.4	37.3				
Fixed Carbon					42.45	28.9	37.96	34.4	29.3				
Ultimate Analysis, mass percent													
C	77.56	64.90	70	67.74	65.36	68.1	64.78	68.4	59.0	59.18	63.99	68.79	67.75
H	5.28	3.65	4	4.29	3.90	4.5	3.95	4.2	3.5	4.08	4.28	5.00	4.50
S	2.00	2.96	2	2.55	2.36	2.3	0.85	0.8	1.1	2.32	2.23	0.60	1.14
N	1.36	1.25	2	1.21	1.43	1.3	1.19	1.0	1.1	0.99	1.13	0.73	0.81
O	3.14	1.70	2	2.91	0.61	1.8	2.57	3.4	1.9		2.58		
Ash	10.66	25.54	20	21.30	25.49	21.0	24.83	21.2	33.4	27.94	25.79	19.91	23.48
Ash Analysis, mass percent													
SiO_2	45.2			43.78	53.49	49.3	44.43	38.4	55.6	47.83		32.61	33.13
Al_2O_3	19.6			15.46	18.76	15.1	22.31	19.4	12.4	18.07		17.70	16.24
Fe_2O_3	25.1			21.80	17.75	20.2	6.67	7.5	6.5	17.81		5.18	8.85
Mn_3O_4													0.09
TiO_2	1.2			0.93	0.94	1.2	1.04	1.5	1.5	0.85		0.88	0.93
P_2O_5	0.5			0.45	0.35		0.92			0.01		0.14	0.56
CaO	2.9			5.32	4.01	5.8	19.20	17.7	12.3	7.40		19.00	15.67
MgO	0.9			3.53	1.05	0.9	4.01	3.4	3.1	0.90		2.80	3.63
SO_3	3.7			3.08	0.0	5.2	0.0	10.3	6.3	3.66		19.39	18.78
Na_2O	0.6			3.22	1.34	1.2	0.77	0.8	0.8	0.45		0.84	0.90
K_2O	1.8			2.42	2.32	1.1	0.66	0.4	0.5	1.81		0.90	0.74
V_2O_5													
NiO													
Boiling Point, °C	–	Vac. Resid.	525°C+	–	525°C+	525°C+	525°C+	525°C+	525°C+	379°C+	Vac. Resid.	344°C+	371°C+
Melting Point, °C		175-190				149-204		149-204	149-204		105-180		
Softening Point, °C				186									
Specific Gravity/°API	1.27/-20.1		1.4/-30		1.491/-36.6		1.313/-23.7						
Molecular Weight													
Viscosity mm^2/s @ °C	2160-18,000 @ 204		10^5 @ 32		Non-		Non-					Non-	Non-
mm^2/s @ °C	300-1240 @ 260		10^3 @ 99		Newtonian		Newtonian					Newtonian	Newtonian
Aromatic Carbon, mass percent													
Aromatic Hydrogen, mass percent													
Insolubles in, mass percent													
Heptane													
Pentane													
Benzene													
Tetrahydrofuran													
Conradson Carbon Residue, mass%					85.57		70.99						
Heating Value, kJ/kg	32,560	26,300	29,075	28,125	27,160	28,820	26,420	28,050	23,710		27,300		
Reference Number	182	183	94	147	184	184	184	184	184	173	183	185	173, 185

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.9 COAL LIQUEFACTION AND COAL TAR (Cont'd)

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985

BY SD

JOB NO. 9041

	Flash Pyrolysis Coal Tar	Flash Pyrolysis Coal Tar											
Pitch Source	Australian	Australian											
	Millmerran	Loy Yang											
	Sub-bituminous	Brown											
Proximate Analysis, mass percent													
Moisture													
Ash	1.2	0.7											
Volatile matter													
Fixed Carbon													
Ultimate Analysis, mass percent													
C	80.6	75.9											
H	7.5	6.3											
S	0.5	0.3											
N	0.8	0.7											
O	10.6	16.8											
Ash													
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3													
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													
MgO													
SO_3													
Na_2O													
K_2O													
V_2O_5													
NiO													
Boiling Point, °C	–	–											
Melting Point, °C													
Softening Point, °C													
Specific Gravity/°API	1.16/-9.4	1.19/-12.2											
Molecular Weight													
Viscosity mm^2/s @ °C	215,500@80	$>10^6$@90											
mm^2/s @ °C	86,200@90												
Aromatic Carbon, mass percent													
Aromatic Hydrogen, mass percent													
Insolubles in, mass percent													
Heptane													
Pentane													
Benzene													
Tetrahydrofuran													
Conradson Carbon Residue, mass%	33.4	41.9											
Heating Value, kJ/kg													
Reference Number	186	186											

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.10 SHALE OIL

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985

BY SD

JOB NO. 9041

Pitch Source	TOSCO Shale Oil 349°C+	TOSCO II Raw Shale Oil	Insitu Retorted Raw Shale Oil	In Situ Retorted Raw Shale Oil	Retorted Green River Shale Oil
Proximate Analysis, mass percent					
Moisture			0.5	Trace	
Ash					
Volatile matter					
Fixed Carbon					
Ultimate Analysis, mass percent					
C	84.65	84.25	84.31	84.66	83.2
H	10.17	11.10	11.87	11.34	11.2
S	0.78	0.81	0.58	0.66	1.23
N	2.97	2.14	1.45	2.18	1.83
O	1.68	1.24	1.79	1.16	1.04
Ash			0.03	0.03	
Ash Analysis, mass percent					
SiO_2					
Al_2O_3					
Fe_2O_3			0.0027 (1)	0.0070 (1)	
Mn_3O_4					
TiO_2					
P_2O_5					
CaO					
MgO					
SO_3					
Na_2O					
K_2O					
V_2O_5					
NiO			0.00065 (1)	0.0002 (1)	
Boiling Point, °C	349-590°C	C_5-515°C+	—	—	—
Melting Point, °C					
Softening Point, °C		24 (Pour)	-4 (Pour)	32 (Pour)	
Specific Gravity/°API		0.928/21.0	0.904/25.0	0.933/20.2	
Molecular Weight	420		279	326	315
Viscosity mm^2/s @ °C			11.1 @ 50	245 @ 50	
mm^2/s @ °C					
Aromatic Carbon, mass percent					
Aromatic Hydrogen, mass percent					
Insolubles in, mass percent					
Heptane					
Pentane					1.0
Benzene					
Tetrahydrofuran					
Conradson Carbon Residue, mass%			0.54	1.85	
Heating Value, kJ/kg					
Reference Number	187	94	188	188	189

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

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DESCRIPTION TABLE 4.11 RETORTING

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985

BY SD

JOB NO. 9041

	Lurgi-Ruhrgas												
Pitch Source	Whole Athabasca Bitumen Feed												
Proximate Analysis, mass percent													
Moisture													
Ash													
Volatile matter													
Fixed Carbon													
Ultimate Analysis, mass percent													
C	84.90												
H	9.15												
S	4.32												
N	0.62												
O	1.01												
Ash													
Ash Analysis, mass percent													
SiO_2													
Al_2O_3													
Fe_2O_3	5 (1)												
Mn_3O_4													
TiO_2													
P_2O_5													
CaO													
MgO													
SO_3													
Na_2O													
K_2O													
V_2O_5	135 (1)												
NiO	45 (1)												
Boiling Point, °C	520°C+												
Melting Point, °C													
Softening Point, °C													
Specific Gravity/°API													
Molecular Weight													
Viscosity mm^2/s @ °C													
mm^2/s @ °C													
Aromatic Carbon, mass percent													
Aromatic Hydrogen, mass percent													
Insolubles in, mass percent													
Heptane													
Pentane													
Benzene													
Tetrahydrofuran													
Conradson Carbon Residue, mass%													
Heating Value, kJ/kg													
Reference Number	96												

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

DESCRIPTION TABLE 4.12 OLEFIN PYROLYSIS

CUSTOMER DEPARTMENT OF ENERGY, MINES AND RESOURCES

DATE December, 1985

BY SD

JOB NO. 9041

	Pyrolysis Fuel Oil	Pyrolysis Residue	Pyrolysis Fuel Oil	Pyrolysis Fuel Oil
Pitch Source	Naphtha Cracking	Naphtha Cracking	Gas Oil Cracking	Gas Oil Cracking
Proximate Analysis, mass percent				
Moisture				
Ash				
Volatile matter				
Fixed Carbon				
Ultimate Analysis, mass percent				
C	91.3	94.3	92.4	92.3
H	7.5	5.5	6.9	7.2
S	1.2		0.7	0.4
N	0.04	0.0	0.08	0.06
O		0.2		
Ash	0.007		0.005	0.004
Ash Analysis, mass percent				
SiO_2				
Al_2O_3				
Fe_2O_3				
Mn_3O_4				
TiO_2				
P_2O_5				
CaO				
MgO				
SO_3				
Na_2O				
K_2O				
V_2O_5				
NiO				
Boiling Point, °C	215-440°C+	270°C+	235-555°C+	210-540°C+
Melting Point, °C				
Softening Point, °C	64		66	38
Specific Gravity/°API	1.12 / -5.2		1.15 / -8.5	1.10 / -2.9
Molecular Weight		1000		
Viscosity mm^2/s @ °C	7612 @ 99		7907 @ 99	16 @ 200
mm^2/s @ °C			36 @ 200	
Aromatic Carbon, mass percent		80 of C		
Aromatic Hydrogen, mass percent		45 of H		
Insolubles in, mass percent				
Heptane				
Pentane				
Benzene		33.6		
Tetrahydrofuran				
Conradson Carbon Residue, mass%	23.2		24.7	
Heating Value, kJ/kg	38,500			39,100
Reference Number	190	181	191	190

(1) Concentration of metallic element in the oil, mg/kg ; (RCR) Ramsbottom Carbon Residue, mass percent

TABLE 4.13

PROCESS LICENSOR CONTACTS

Process Licensor	Processes	Results
Chevron Research Company	Residuum Hydrodesulphurization	- data provided are in Table 4.3, Reference 168
Exxon Research and Engineering Company	EDS Coal Liquefaction	- data provided are in Table 4.9, Reference 184
	Residuum Hydrodesulphurization	- data requested were not available as they are not usually measured
Gulf Canada Limited	Donor Refined Bitumen	- data from typical operation are not available since the process is under development
	Residuum Hydrodesulphurization	- data for Gulf process not available through Gulf Canada - the Gulf process was included in the data provided by Chevron
Hydrocarbon Research Inc.	H-Oil	- data provided are in Table 4.4, Reference 173
	H-Coal	- data provided are in Table 4.9, Reference 173
M.W. Kellogg Co.	Asphalt Residuum Treating	- only a small amount of 525°C+ is produced and it can be processed with the heavy gas oil in conventional refinery units
	Fluid Catalytic Cracking	- data provided are in Table 4.8, Reference 179
Kerr-McGee Corporation	ROSE Solvent Deasphalting	- data provided are in Table 4.7, Reference 178
Lummus Crest Inc.	LC-Fining	- data provided are in Table 4.4, Reference 175

TABLE 4.13 (Cont'd)

PROCESS LICENSOR CONTACTS

Process Licensor	Processes	Results
Mitsui & Company	Eureka	- data provided are in Table 4.5, Reference 176
Partec Lavalin Inc.	CANMET Hydrocracking	- pitch quantities large enough for detailed analysis will not be available until the demonstration plant is operating - they are working on the removal of particulates from the pitch to give it a wider potential end use
Stone & Webster	Olefin Pyrolysis	- data provided are in Table 4.12, Reference 190
Union Oil Company	Residuum Hydrodesulphurization Shale Oil Process	- insufficient manpower to give us any data
UOP Inc.	Solvent Deasphalting	- data provided are in Table 4.7, Reference 12
	Fluid Catalytic Cracking	- no data provided
Veba Oel	Veba Combi-Cracking	- they have generated pitch data for internal use only that are not for publication - data are available by buying the AOSTRA Upgrading Residue Utilization Project results

P.R. #9041.14
File #9041.2

SECTION 5.0 - CONCEPTUAL DESIGN DISCUSSION OF LABORATORY TEST UNIT FOR THE CANMET PITCH PYROLYSIS/GASIFICATION PROCESS

5.0 CONCEPTUAL DESIGN DISCUSSION OF LABORATORY TEST UNIT FOR THE CANMET PITCH PYROLYSIS/GASIFICATION PROCESS

This section presents a discussion of the options for a laboratory test unit for the catalytic pitch pyrolysis and gasification processes being developed by CANMET. The scope of work for the project defines this as a conceptual design rather than an engineering design so that detailed drawings and calculations for use in constructing the test unit were not to be prepared. Block flow diagrams of the pyrolysis and gasification test units are given showing the individual components proposed for the plant. The definition of the process parameters and required range of operating variables are not firm enough at this time for all the equipment items to be specified. For most components the available options are discussed. Where there is sufficient definition, the description of the function, capacity, construction material, and commercial availability of the component is given. In most cases there is not sufficient laboratory data for this to be done. This technical proposal must be reviewed by CANMET and discussed before a final test unit design can be prepared for construction during the next phase of this project.

5.1 Previous Experimental Work by CANMET

CANMET's work on the pitch pyrolysis and gasification processes was begun in 1977 by M. Ternan and M. Sekhar. The work originated from a desire to convert the 10% pitch waste from the CANMET hydrocracking process for maximum liquid fuels production. The initial pyrolysis test work was done on small scale, batch, thermogravimetric balance equipment. Pitch samples up to 100 mg were pyrolyzed in an inert atmosphere of helium or nitrogen. Results from pyrolysis of pitch from hydrocracked Athabasca bitumen have been reported without the use of catalyst (61) and with gamma alumina catalyst (62). This work was discussed in Sections 3.3.1 and 3.3.2. At about 500°C, non-catalytic pyrolysis produced 6 mass percent gas, 23 mass percent liquid product and 71 mass percent coke residue. The use of catalyst doubled the gas yield, raised the liquid product yield to 26 mass percent and reduced the residual coke yield to 62 mass percent. Larger samples of up to 10 g were pyrolyzed by Furimsky (60) in a modified Fischer retort.

Ternan and Sekhar used the thermogravimetric balance equipment to measure the gasification rate with steam of the residual coke or char from the pyrolysis reaction (156, 157). Tests were done in an atmosphere of nitrogen and water vapour without catalyst and with either potassium carbonate or vanadium pentoxide catalyst. It was found that potassium carbonate enhanced the gasification rate while vanadium pentoxide inhibited gasification compared to the non-catalytic rate. No data have yet been generated for the gasification reaction with both steam and oxygen so gas compositions and conditions in the gasification reactor test unit are not directly known.

CANMET presented additional unpublished experimental results during the Task 3 Kickoff Meeting (193). An additional series of 27 pyrolysis tests was run on the modified Fischer retort which was gradually heated from room temperature to 500°C with up to 40 g of pitch. Most of the runs used gamma alumina catalyst and evaluated different catalyst to pitch ratios and operating conditions. The conclusions from this work were:

- At a final temperature of 500°C, the product yields were 24 mass percent liquid, 18 mass percent gas and 58 mass percent residual coke.

- The reaction time required to recover the liquid product and over 90 percent of the gas was 30 minutes or less.

- The use of catalyst increases the gas yield but may not increase the liquid yield. It does, however, improve the liquid quality with more carbon and hydrogen, less sulphur, oxygen and nitrogen, and a lower boiling point curve.

- A catalyst to pitch feed ratio of 20:1 or higher was required to eliminate agglomeration of the catalyst during reaction.

CANMET also reported on work with a larger scale continuous fluidized bed pyrolysis reactor. The reactor was designed to pyrolyze 10 - 50 g/h of pitch feed at up to 600°C with nitrogen as a carrier gas. The unit experienced a number of problems and was never operated successfully. The major problems experienced were:

- inability to maintain a uniform liquid pitch feed rate

- inlet blockage when the feed was changed to solid pitch

- agglomeration of catalyst particles during pyrolysis due to the sticky nature of the pitch
- difficulty in maintaining makeup catalyst flow against the reactor back pressure.

After 9 - 12 months of unsuccessful operation, it was decided by CANMET that quantitative measurements could not be made on the continuous fluidized bed and work shifted to the batch testing on the modified Fischer retort reported above.

5.2 Test Unit Objectives

The overall objective of the laboratory test unit is to develop the process and engineering data needed for an evaluation of the process and for the future design of a pilot or demonstration plant. Key aspects of this are the development of the bifunctional catalyst and an understanding of the reaction mechanisms of pyrolysis and gasification. The specific data requirements defined by CANMET (194) are:

- ability to vary the operating conditions and catalyst composition
- measurement of product yields for a material balance
- determination of boiling curve, CHONS analysis and density for the liquid product, and component analysis for the gas product. This requires production of about 100 cm^3 of pyrolysis liquid product.

Additional requirements for the test unit are that it operate on a continuous basis and produce the 100 cm^3 liquid sample from a steady state experiment that is completed in one shift of 7.5 hours. An important objective of the test unit is to define the susceptibility of the bifunctional catalyst to poisoning and deactivation. The unit must be able to process a range of different pitches as defined in Section 4.0.

The pyrolysis and gasification test units are to operate as completely independent systems to facilitate the development of basic process and kinetic data. Integrated operation would be deferred until a basic understanding of the process and catalysts has been achieved.

CANMET wants to allow for this research work to be contracted out and, therefore, requested that the subsequent engineering design of the test unit provide a modular design to allow portability. They also requested that there be no welded joints in the reaction system so that it can be taken apart and reassembled in about 1 hour. These objectives are requirements for the engineering design and not the conceptual design presented in this report.

5.3 Particle Agglomeration and Reactor Types

Section 5.1 outlined some of the problems due to pitch stickiness and particle agglomeration that made the operation of the previous continuous fluidized bed pyrolysis reactor unsuccessful. Similar problems have been reported by other researchers.

Kono (195) says that particle agglomeration can result from:

- a high ratio of liquid amount in the bed:solid particle holdup in the bed

- a low bed mixing rate

- the liquid properties and rate of pyrolysis.

The absolute values at which agglomeration will occur depend on the individual system.

A high rate of bed circulation will provide uniform liquid distribution and break up agglomerates that may form. Zenz (196) derived a correlation for the internal solids circulation rate based on industrial situations where a high degree of solids uniformity was essential. He found that the circulation rate was a function of the difference between the superficial fluidizing velocity and the minimum fluidizing velocity. High fluidizing velocities are, therefore, desirable for the pyrolysis reaction.

Kono (195) considered a spouted bed but felt that since the annular part moved like a moving bed it would not provide enough circulation for application to potentially agglomerating systems. He is instead developing a combination spouted-fluidized bed to improve circulation. He gives examples for the spouted-fluidized bed where agglomeration did not occur in one case until the gas velocity was less than two times the minimum fluidizing velocity and in another case until the mean residence time of the solid particles in the bed fell below 30 minutes.

Watkinson et al (197) have studied steam-air coal gasification of both caking and non-caking coals in a fluidized bed and a spouted bed. It was hoped that the spouted gasifier would prevent agglomeration with caking coals by providing good circulation and having no distributor grid for agglomerates to build up on. They found, however, that there were no significant advantages with the spouted bed as the use of inert bed materials allowed the use of either reactor with caking coals. The inerts reduced the volume fraction of sticky particles sufficiently for stable operation. Zenz and Othmer (198) give a similar example of a fluidized bed carbonizer that used 10 parts recycle coke to 1 part of feed coal to prevent caking coals from agglomerating. This is the same effect as going to a higher solids:oil ratio with a liquid feed. It may be concluded from the work of Kono, Watkinson et al and Zenz and Othmer that a fluidized bed should perform as well as a spouted bed in an agglomerating system if a sufficiently high solids:feed ratio is used.

The fluidized bed pyrolysis of whole Utah tar sand has been reported by Dorius et al (199). They used a reactor 3.8 cm diameter by 90 cm high at about 550°C with nitrogen as a fluidizing gas to give a superficial fluidizing velocity of about 12 cm/s. The average retention times of sand in the bed ranged from about 6 to 20 minutes. Two of the three tar sands gave successful operation but the third agglomerated and formed a bridge of coke across the reactor. The bridging was attributed to the high asphaltene content of the bitumen and the sticky nature of the coke precursors on the sand surface. The following ratios were calculated for the three tar sands with South being the sand that formed the bridge across the reactor.

Mass Ratios	South (Agglomerated)	Rainbow I	Rainbow II
Coke/Sand	0.0172	0.0198	0.0187
Conradson Carbon/ Sand	0.0165	0.0231	0.0162
Asphaltene/Sand	0.0571	0.0855	0.0559
Bitumen/Sand	0.0689	0.165	0.0933

Since these parameters do not show a trend that explains the agglomeration, the liquid properties must be playing a role. Data reported from fluidized bed pyrolysis of Athabasca bitumen by Gishler and Peterson indicate that they achieved successful operation with a coke/sand ratio of about 0.0164 (99). Results from CANMET'S fluidized bed pyrolysis reactor, given in Section 5.1, suggest that significant agglomeration occurred at a pitch to solids ratio above 0.05 which is equivalent to a coke to solids ratio of about 0.035. Yan and Shu (200) have recently reported data for pitch pyrolysis on coal in a fluidized bed with a coke to solids ratio of about 0.033. While there are other factors involved, these results suggest that a fluidized pyrolysis unit should be capable of operation with a coke/solids ratio of 0.02 or less to prevent agglomeration.

Veba Oel has given a brief outline of a Low Temperature Carbonization process (Section 3.3.1 (i)), in which residual pitch is pyrolyzed in a rotary kiln (103). No details are given of the kiln or the internals needed to prevent an accumulation of coke on the walls. A kiln reactor is not recommended for the small throughput laboratory test unit for CANMET. The operation of the kiln and internals would be too complex on the small laboratory scale and would detract from the catalyst development and understanding of the reaction mechanism that are the object of the laboratory test unit.

CANMET asked that the use of a riser reactor be evaluated for pyrolysis. Hatch Associates does not feel that a riser reactor is a practical option when a catalyst retention time in the reactor of up to 30 minutes has been specified by CANMET. A riser with this solid retention time would either have a vapour product residence time of about 15 minutes with a slip ratio of 2 or would need to have a complex system of gas-solid separators to give low gas product residence times.

The long vapour residence time would result in almost complete degradation by secondary reactions and the separator option is not considered to be practical.

In riser processing, high velocities are required to maintain a uniform dispersion of reactants (198) which will result in a very long reactor if the reaction rate is not fast. CANMET had asked Hatch to investigate the use of very small catalyst particles and low gas transport velocities to minimize the riser reactor length but the low velocities would not provide sufficient turbulence and mixing to distribute the pitch feed uniformly over the solid catalyst. The use of a riser is, therefore, not recommended for the laboratory test unit.

The advantage of a riser reactor is to provide plug flow with a minimum of backmixing for a fast reaction such as fluid catalytic cracking where the riser reaction time is about 2 seconds. Skubnik (201) at CANMET has done a preliminary design of a riser reactor using a mathematical model based on the limited batch test work done at CANMET. His riser designs allowed for residence times of 2 -10 s at 500 - 700°C in lengths of 10 - 40 m which do not come close to providing the solids retention time specified by CANMET for this project without the use of a substantial recycle solids stream which would then approach fluidized bed operation in general concept. Additional kinetic data that would be developed from the laboratory test unit are needed before such short reaction times can be modelled for a short riser design.

In summary, the riser and kiln reactor options are not recommended. The spouted reactor in other agglomerating applications has not shown an advantage over a fluidized bed with a high solids:feed ratio. Because of its proven use and relative simplicity of operation, the use of a fluidized bed is recommended for both the pyrolysis and gasification reactors in the laboratory test unit to develop basic information about process conditions, reaction mechanisms and catalysts. There are several Canadian researchers presently developing novel reactor systems in this field as outlined below.

Sumner et al (202) at the University of Western Ontario are studying the Ultra-Rapid Fluidized (URF) Pyrolysis process. Carbonaceous feeds are rapidly pyrolyzed at high temperature (900°C) and then rapidly quenched resulting in very short residence times of about 0.5 s. They are presently doing kinetic studies of a biomass feed and cold modelling of the reactor system.

Stocker et al (203) have been studying heat transfer in spout-fluid beds with and without a draft tube at the University of Calgary. They suggest that for fast, endothermic reactions such as high temperature pyrolysis, the spout may be the most significant region of the reactor in providing gas-solid contact with extremely short contact times. The reactor system has been used for propane pyrolysis and is being developed for further pyrolysis applications but these details have not yet been made public.

Scott et al at the University of Waterloo (204) have developed a fluidized bed reactor for pyrolysis with the initial development on cellulosic biomass. They use a fluidized sand bed at atmospheric pressure and 400 - 650°C. The product vapour has a residence time in the bed of about 0.5 s. The sand acts as a heat carrier and they have done some work with catalyts. A unique aspect of their bed is operation in a "blow through" mode where the char is blown from the bed while the sand is retained. The char is collected from the product gas by a cyclone and the sand particles do not need to be separately regenerated.

Since the novel aspect of CANMET's process is the use of a bifunctional catalyst for pitch pyrolysis and char gasification it is recommended that discussions be held with these researchers to determine the possibility of developing the catalytic pitch conversion process on one of the new reactors.

5.4 Pyrolysis Reaction Test Unit

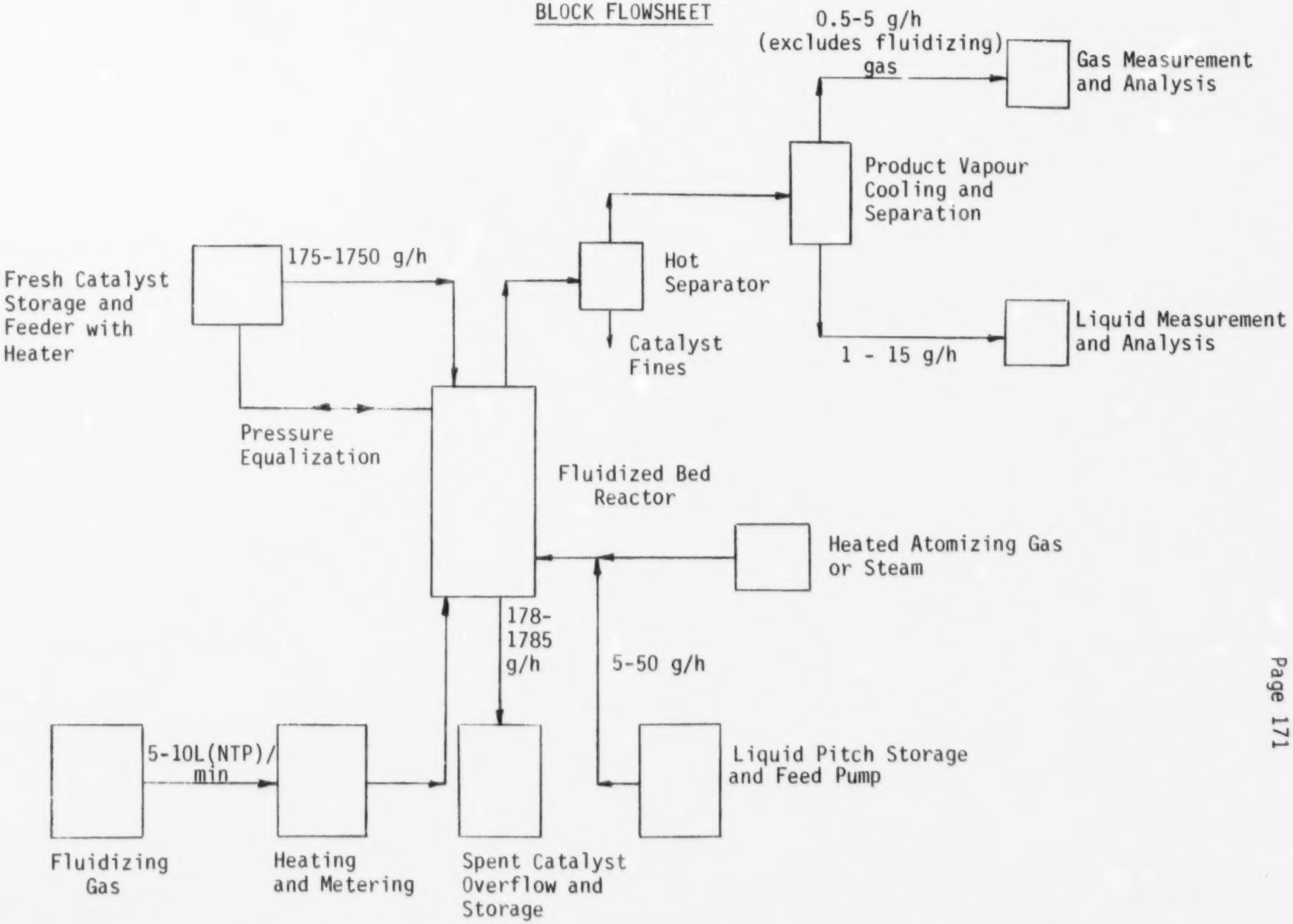
5.4.1 Conceptual Flowsheet

In general concept, the block flowsheet of the pyrolysis reaction laboratory test unit given in Figure 5.1 is the same as the unit previously tested by CANMET (193). There are, however, a number of improvements suggested as well as operating parameter changes and concerns discussed in Section 5.4.2 and potential heat balance problems discussed in Section 5.4.3.

FIGURE 5.1

PYROLYSIS REACTION LABORATORY TEST UNIT

BLOCK FLOWSHEET


0.5-5 g/h
(excludes fluidizing)
gas
Gas Measurement
and Analysis
Product Vapour
Cooling and
Separation
175-1750 g/h
Fresh Catalyst
Storage and
Feeder with
Heater
Hot
Separator
Catalyst
Fines
Liquid Measurement
and Analysis
1 - 15 g/h
Pressure
Equalization
Fluidized Bed
Reactor
Heated Atomizing Gas
or Steam
178-
1785
g/h
5-50 g/h
5-10L(NTP)/
min
Liquid Pitch Storage
and Feed Pump
Fluidizing
Gas
Heating
and Metering
Spent Catalyst
Overflow and
Storage

A fluidizing gas which could be nitrogen or steam is heated to the reactor temperature and metered into the bottom of the fluidized bed. Liquid pitch is pumped from storage and mixed with heated atomizing gas or steam before being fed into the fluidized bed. The feed will be to the centre of the bed where the rapid solids motion will promote adequate pitch dispersion. The solids mixing will be maximized by operating with as high a superficial fluidizing velocity as possible. The use of solid pitch feed should not be an advantage over liquid feed since in both cases effective dispersion caused by fluidized solid mixing is the essential factor to avoid agglomeration.

The fluidized bed can be fabricated of stainless steel as before or ceramic as later suggested by CANMET (194). The reactor will be heated externally with an electric heater. The sintered plate used previously as the bed support and gas distributor may have been susceptible to plugging and it is suggested that a perforated plate with circular holes be used. The initial gas bubble size in the fluidized bed is a function of the gas velocity through the grid openings. The initial bubbles will grow by merger until they are restricted by the diameter of the laboratory scale fluidized bed at which point the bed changes to slugging flow. Since the solids circulation is less intense in slugging flow, it is desirable to have smaller initial bubbles from the pyrolysis reactor grid. The grid and fluidized bed design will be based on references such as Zenz (196) after the final design basis has been established by CANMET.

Spent catalyst will overflow through a standpipe from within the fluidized bed to a storage pot for later analysis. If the fluidized bed is operated without solids agglomeration, stainless steel tubing should work well for the catalyst overflow.

Fresh catalyst is fed from storage through a screw feeder or star valve to the top of the fluidized bed. A pressure equalization line is required to ensure that the feeder is not working against reactor back pressure. A screw feeder should work well with proper pressure equalization. Since the future process will likely involve the use of hot regenerated catalyst from the gasification reactor as a source of heat for pyrolysis, the catalyst feed system should be capable of supplying makeup catalyst heated to as high as 800-900°C.

An alternate system for catalyst feed and overflow would involve the use of weirs, fresh catalyst entering on one side and flowing under a weir into the bed and spent catalyst leaving from the other side by overflowing a weir. This system would minimize fresh catalyst bypassing through the bed.

The product vapour will flow to a hot separation vessel for removal of entrained catalyst fines. The product is then cooled and separated for analysis of the gas and liquid fractions.

5.4.2 Operating Parameters

CANMET's guidelines (194) for the pyrolysis test unit require that it be capable of processing a pitch feed rate range of 5 - 50 g/h. One of the objectives of the test unit defined in Section 5.2 is to produce 100 cm^3 of liquid product from a run completed over one shift. The liquid yield will be about 25 mass percent based on previous CANMET results. If the liquid is produced from 6 hours of steady state operation, a pitch feed rate of 59 g/h is required to produce 100 cm^3 of liquid. If the steady state operating period is 5 hours, a pitch feed rate of 71 g/h is required. The feed rate range, test duration and product volume requirements specified by CANMET must be coordinated. The following calculations use the 5-50 g/h range specified in the guidelines.

Based on the previous test work discussed in Section 5.1, the maximum coke (char) yield will be about 70 mass percent resulting in a coke product of 3.5 - 35 g/h. As discussed in Section 5.3, the catalyst addition rate should be capable of maintaining the coke to solids mass ratio at 0.02. The required catalyst makeup rate is, therefore, 175 - 1750 g/h which is much higher than the 10-200 g/h range given in CANMET's guidelines. Based on the experimental data in Section 5.3, the 175 - 1750 g/h makeup range must be allowed in the design of the fluidized bed to minimize agglomeration.

The guidelines ask that the solids retention time in the fluidized bed be capable of variation from 1 - 30 minutes. The resulting bed weights for the range of retention times across the range of catalyst feed rates is given in Table 5.1. With a fluidized bed expansion of two times, the bed density

TABLE 5.1

PYROLYSIS REACTOR BED SIZE

	Bed Weight at Solids Retention Time, min		
Catalyst Feed Rate, g/h	1	10	30
175	2.9 g	29 g	87.5 g
1750	29 g	290 g	875 g

	Bed Volume at Solids Retention Time, min		
Catalyst Feed Rate, g/h	1	10	30
175	8.3 cm^3	83 cm^3	250 cm^3
1750	83 cm^3	830 cm^3	2500 cm^3

will be 0.35 g/cm^3 which results in the bed volumes given in Table 5.1. The guideline specifies a reactor size of 5.0 cm diameter by 75 cm high. If the bed height within the reactor were 40 cm, the bed volume would be 785 cm^3 which would provide a retention time of only 9.5 minutes at the maximum catalyst makeup rate. A fluidized bed 8 cm diameter by 50 cm high is required for a 30 minute retention time with 1750 g/h catalyst makeup. This would result in a reactor 8 cm diameter by 90 cm high.

The solid catalyst specified (193, 194) has a minimum particle diameter of 44 μm, mean particle diameter of 65 μm and maximum particle diameter of 250 μm. The minimum fluidizing velocity was calculated for estimated pyrolysis reactor conditions at 500°C and 1 atmosphere pressure. Several correlations were used including a derivation of the Ergun equation (205), Kunii-Levenspiel (206), and Baeyens and Geldart (206). The difficulty in using generalized correlations is in estimating both the bed porosity at the point of minimum fluidization and the particle shape factor. With a bed porosity of 0.55 at minimum fluidization and a shape factor of 0.7 (206), minimum fluidizing velocities of about 0.2 cm/s were calculated. With a porosity of 0.7 at minimum fluidization (198), the calculated minimum fluidizing velocity is about 1 cm/s. Kirk-Othmer (207) gives minimum fluidizing velocities of 0.3 - 0.9 cm/s for fluid catalytic cracking catalyst (10 - 200 μm) which would be similar to the catalyst under consideration. This is within the range of the calculated values. The incipient bubbling velocity is the point at which gas bubbles form in the bed and is more significant for reactor design. Kirk-Othmer gives a range of 3 - 9 cm/s for catalytic cracking catalyst.

Correlations were used (198, 206) to calculate the gas velocity required to give a bed expansion of 2. The results are not useful as they showed wide scatter of from 11 to 41 cm/s. The fluidized bed in a typical fluidized catalytic cracker regenerator operates with a superficial gas velocity of about 70 cm/s but has cyclones for returning entrained catalyst fines to the bed. The generalized fluidization correlations cannot provide accurate design data for a new system when porosity and particle data are not known. Kirk- Othmer (207) notes that the optimum superficial fluidizing velocity is most frequently based on pilot plant test experience. Since providing good bed mixing is most important to prevent agglomeration in this application, it is recommended that CANMET do velocity, pressure drop and bed expansion tests with the proposed catalyst in a glass column with a perforated gas distributor. The data generated will ensure that the design superficial velocity provides sufficient solids mixing.

A laboratory reactor velocity of about 12 cm/s was used by both Dorius et al for tar sands pyrolysis (199) and by Yan and Shu (200) for pitch pyrolysis on ground coal (150 - 300 μm). This value can, therefore, be used as a preliminary estimate of the superficial fluidizing velocity required in the pyrolysis reactor. Stokes law was used to calculate entrainment velocities of particles from the bed. At 12 cm/s all particles smaller than about 78 μm will be carried from the bed. This represents 65% of the catalyst. To keep the smallest 44 μm particles in the bed, the superficial velocity would have to be held below 3.8 cm/s. Since this may not be much above the minimum bubbling velocity for the bed, the importance of the basic fluidization tests suggest above is reemphasized.

A superficial velocity of 12 cm/s would require a fluidizing gas feed rate of 5 L (NTP)/min in a 5 cm diameter reactor at 500°C. This compares to the 0.5 - 10 L(NTP)/min rate specified by CANMET. The higher flows may be needed at lower pyrolysis temperatures but flows at the lower end of the range are unlikely to provide sufficient velocity (1.2 cm/s at 0.5 L/min) for adequate fluidization with the pitch feed. The range of fluidizing gas flows can only be set after the superficial fluidizing velocity and bed diameter have been determined.

The guidelines given by CANMET (194) can be revised as follows, based on the above discussion:

Bitumen pitch - Feed rate 5 - 50 g/h (up to 71 g/h to produce 100 cm/^{3} liquid product in 5h)
- Feed temperature 250 ± 15°C
- Melting temperature 100°C

Catalyst - 44 μm to 250 μm (some smaller sizes may be removed depending on fluidization tests)
- Feed rate 175 - 1750 g/h
- Bulk density 0.7 g/cm^3

Reactor size	- 8 cm diameter by 90 cm high for 30 minute retention time with 1750 g/h catalyst rate
Solids retention time	- 1 to 30 minutes
Fluidizing gas, N_2	- flow to be determined after fluidization tests and confirmation of reactor size
Reactor conditions	- 300 - 700°C - Atmospheric pressure
Test duration	- One shift, 5 - 6 h at steady state.

5.4.3 Heat Balance

The relatively high catalyst flows that may be necessary to prevent agglomeration will have a significant impact on the concept of operating the process commercially on the same basis as a fluid catalytic cracker. In this application, the pyrolysis and gasification units would be integrated with the heat for pyrolysis being provided by hot catalyst from the gasifier. A heat balance was done for a pyrolysis reactor at 500°C with pitch and fluidizing gas fed at 250°C. The weight ratios of feeds, based on the calculations in Section 5.4.2 are 7.3 kg nitrogen per kg pitch and 32.5 kg catalyst per kg pitch. The resulting heat balance calculated the required hot catalyst temperature from the gasifier at 585°C in order to satisfy the pyrolysis reactor heat balance. If the catalyst ratio were cut in half, the required hot catalyst temperature would become 670°C. Since the gasifier operating temperature will be in the 800 - 1000°C range, it may not be feasible to integrate these units in a manner analogous to a fluid catalytic cracker. Heat would have to be removed from the hot gasifier catalyst before the pyrolysis unit.

5.4.4 Feed and Product Systems

Maintaining uniform flows of pitch and fresh catalyst to the fluidized bed is important in preventing agglomeration from occurring. The difficulties that CANMET experienced with these feeds to the earlier continuous fluidized bed pyrolyzer likely contributed to the agglomeration problem.

Solids have been successfully fed to fluidized beds in the past using screw feeders (99, 199, 200) and a screw feeder is recommended for feeding catalyst to the pitch pyrolysis reactor. Pressure equalization must be provided between the reactor freeboard and the solids feed system if a uniform feed rate is to be maintained. This will ensure that the feeder is not operating against a backpressure.

The solids heater will be assessed during the engineering design phase. The use of hot makeup catalyst should minimize the occurance of lower temperature regions in the bed that could make the pitch stickier and lead to agglomeration.

CANMET had difficulty maintaining liquid pitch feed to the previous fluidized bed when a Ruska piston pump was used. They switched to feeding solid pitch but had difficulty with plugging and had to water cool the inlet. Hatch Associates considers that liquid pitch can be successfully fed to the fluidized bed and recommends that that option be developed into a workable system. The solid feed option provides no advantage in minimizing potential agglomeration and would not be as simple to operate as a pump. The pump vendors who should be consulted are:

- D.B. Robinson and Associates in Edmonton.
  They manufacture Ruska pumps for heavy oil applications.

- Milton Roy Industries who have provided pumps to the Alberta Research Council for bitumen applications.

- Hydro Dynamics Ltd. in Toronto.
  Hatch Associates recently observed a pilot plant run where a Bran and Lubbe positive displacement pump was feeding 200°C pitch to an atmospheric pressure reactor.

The fluidizing gas fed to the reactor should be preheated to reactor temperature as another means of preventing agglomeration.

CANMET had difficulties with the product outlet lines plugging on their earlier fluidized bed reactor. Syncrude had the same difficulty with a laboratory unit for pyrolysis of tar sand (99). They designed the vapour outlet line with a plunger so that it could be manually cleared of coke during a run. The use of two vapour outlet lines, both with manual decokers, should be included in the design of the pyrolysis reactor.

It was recommended in Section 5.4.1 that the spent catalyst outlet be a straight piece of tubing. If non-agglomerating conditions are maintained, this should provide adequate solids flow. Syncrude (99) found their solid outlet plugged only when the reactor residence time was less than 2 minutes. An alternative arrangement would be for the spent catalyst to overflow a weir at the side of the reactor. Being close to a wall, this would facilitate access for cleaning.

5.5 Gasification Reaction Test Unit

5.5.1 Conceptual Flowsheet

The block flowsheet of a proposed gasification reaction laboratory test unit is given in Figure 5.2. The unit is similar in overall concept to the pyrolysis reaction test unit block flowsheet presented in Section 5.4.1. Some of the operating parameters proposed by CANMET (194) are discussed in Section 5.5.2.

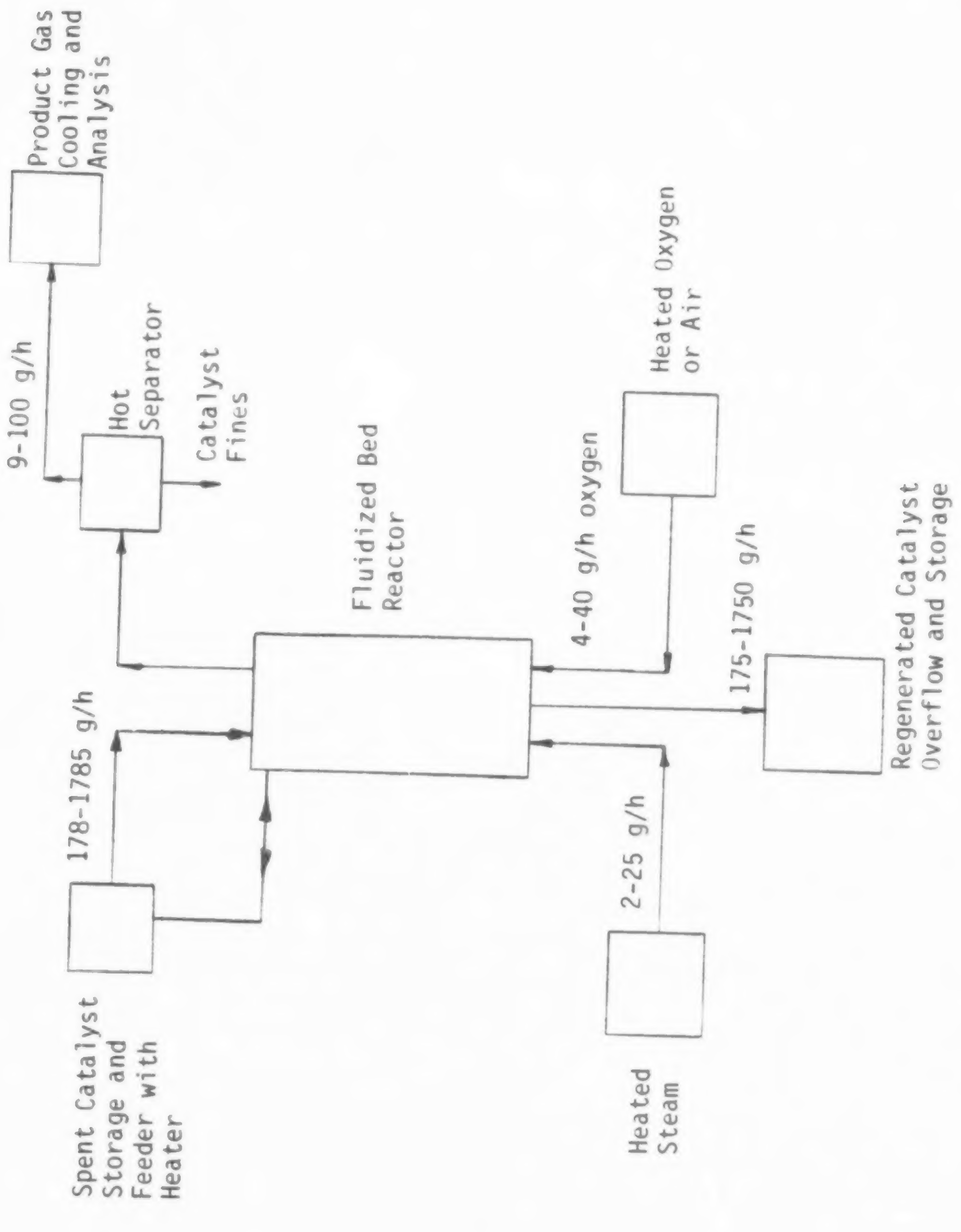
Steam for the gasification reaction is preheated and added to the bottom of the fluidized bed reactor. Preheated oxygen or air is also added as both a fluidizing gas and an oxidant to partially combust the char on the spent catalyst. The heat from the partial combustion maintains the gasification reactor heat balance and the reactor bed temperature. A heating jacket will be placed around the reactor to allow greater operating flexibility. The amount of air or nitrogen added to the oxygen will depend on the balance between the requirements for fluidizing gas velocity to maintain good bed mixing and combustion/heat balance to maintain the bed temperature.

The material selection for the gasification reactor at the specified temperatures of up to 1200°C is more difficult than for the pyrolysis reactor. The choices are a refractory lined steel reactor, a reactor fabricated of a high Ni - Cr alloy or a ceramic reactor. The evaluation and selection from those options will be part of the detailed design phase. The temperature control on the gasification reactor will have to be carefully designed to prevent high temperature excursions

FIGURE 5.2

GASIFICATION REACTION LABORATORY TEST UNIT

BLOCK FLOWSHEET


Spent Catalyst Storage and Feeder with Heater
178-1785 g/h
Fluidized Bed Reactor
Hot Separator
Catalyst Fines
9-100 g/h
Product Gas Cooling and Analysis
Heated Steam
2-25 g/h
Heated Oxygen or Air
4-40 g/h oxygen
175-1750 g/h
Regenerated Catalyst Overflow and Storage

caused by possible imbalance between spent catalyst feed rate and oxygen feed rate.

The spent coked catalyst from the pyrolysis reaction test unit is fed from storage through a screw feeder or star valve to the top of the fluidized bed. As with the pyrolysis reactor, a pressure equalization line is required to ensure that the feeder is not working against reactor back pressure.

The regenerated catalyst is produced from the reactor through a standpipe from within the fluidized bed to a storage pot for later analysis.

A weir system for catalyst feed to and overflow from the bed would also be considered as a means of controlling the level of the fluidized bed.

The product vapour flows to a hot separator for removal of entrained catalyst fines. The product is then cooled and analyzed.

In the pyrolysis reactor it was important that the fluidized bed provide effective solids mixing to provide uniform pitch distribution and prevent agglomeration. In the gasification reactor, the bed must provide good contact between the fluidizing gas and the solids for the gasification reactions to proceed rapidly. This should be readily accomplished because small scale fluidized beds are more efficient gas- solid contactors than commercial size reactors. This is because:

- the smaller grid holes result in smaller initial bubble sizes.
- the largest bubble size is limited by the reactor diameter.
- once slugging flow has been established there is excellent gas-solid contact because all the solids above the slug size bubble must descend in a downflowing shell at the tube wall.

Contrary to the pyrolysis reactor case, it may be desirable to have some slugging flow in the gasification reactor. The gasification reactor grid and fluidized bed design will be based on references such as Zenz (196) after the final design basis has been established by CANMET.

5.5.2 Operating Parameters

CANMET's guidelines (194) for the gasification test unit require that it be capable of processing a spent catalyst feed rate range of 10 - 250 g/h. However, in Section 5.4.2, it was shown that the spent catalyst production rate from the prolysis reactor may be 175 - 1750 g/h to prevent agglomeration. Since one object of the test program will be to test the catalyst through several pyrolysis-gasification cycles, the gasification reactor would preferably have a solids feed capacity of 175 - 1750 g/h.

The guidelines ask that the solids retention time in the fluidized bed be capable of variation from 1 - 500 minutes. Hatch Associates considers the upper end of this range to be excessive for reactions occurring at temperatures up to 1200°C. The somewhat analogous fluid catalytic cracking regenerator operates at 700°C with a catalyst retention time of about 5 - 10 minutes. It is felt that a maximum catalyst retention time of 30 minutes, as used for the pyrolysis reactor, should be adequate for the gasification test unit. The resulting bed weights for the range of retention times across the range of spent catalyst feed rates is given in Table 5.2. Since agglomeration will not be a problem in this reactor, the superficial fluidizing velocity may not need to be as high as in the pyrolysis reactor. A bed density of 0.5 gm/cm^3 has been assumed which results in the bed volumes given in Table 5.2. The guideline specifies a reactor size of 5.0 cm diameter by 75 cm high. If the bed height were 40 cm, the bed volume would be 785 cm^3 which would provide a retention time of 13.5 minutes at the maximum catalyst feed rate. A fluidized bed 7 cm diameter by 45 cm high is required for a 30 minute retention time with 1750 g/h catalyst feed rate. This would result in a reactor 7 cm diameter by 85 cm high.

As noted in Section 5.1, CANMET has not done any test work using both steam and oxygen for gasification. Without having data for the product gas composition at different gasification conditions, it was necessary to estimate a gasifier material balance using data from other sources. The calculation was based on the same mass flow ratios as for the reactor heat

TABLE 5.2

GASIFICATION REACTOR BED SIZE

Catalyst Feed Rate, g/h	Bed Weight at Solids Retention Time, min			
	1	10	30	500
175	2.9 g	29 g	87.5 g	1458 g
1750	29 g	292 g	875 g	14,583 g

Catalyst Feed Rate, g/h	Bed Volume at Solids Retention Time, min			
	1	10	30	500
175	5.8 cm^3	58 cm^3	175 cm^3	2920 cm^3
1750	58 cm^3	583 cm^3	1750 cm^3	29,170 cm^3

balance in Section 5.4.3 with a 65 mass percent coke yield. The data published by CANMET show that the steam gasification reaction follows:

$$C + H_2O \longrightarrow CO + H_2$$

since the CO/H_2 ratio tended to 1 as the temperature rose from 600 to 800°C. The overall gasification reaction is analogous to Exxon's Dual Gasification Flexicoking process (93) where there are separate vessels for steam-coke gasification and air-coke gasification. Exxon's data show that the air gasification reaction produces gas with a CO_2 to CO ratio of about 1. Using the above values with calculated heats of reaction, a material and heat balance was estimated by Hatch Associates for the fluidized bed gasifier with steam and oxygen. Based on 1 kg of pitch, the calculated gasifier feeds were:

0.65 kg	coke at 500°C
32.5 kg	catalyst at 500°C
0.45 kg	steam at 150°C
0.70 kg	oxygen at 150°C

and the products were:

32.5 kg	catalyst
1.11 kg	CO at 760°C
0.64 kg	CO_2 at 760°C
0.05 kg	H_2 at 760°C

Sufficient heat was added to the catalyst for the pyrolysis heat of reaction. The coke reaction was 54 percent with oxygen to maintain the gasifier heat balance and 46 percent with steam to produce synthesis gas components. If the catalyst were fed to the laboratory reactor at room temperature, there would not be sufficient coke to heat it to reaction temperature even if no steam gasification were done. This will require that either the reactor have an external electric heater or the spent catalyst must be preheated before being fed to the gasification reactor. The external heater is the preferred option.

The product gas from the fluidized bed was calculated for a coke feed rate of 35 g/h, equivalent to about 50 g/h of pitch to the pyrolysis reactor. The resulting gas rate was 1.6 L(NTP)/min which would give a velocity of about 5 cm/s at 760°C in a 5 cm diameter reactor. This may not be sufficient for adequate fluidization but the fluidization test discussed in Section 5.4.2 must be done before this can be determined. If additional fluidizing gas is required, the use of steam should be considered since it is easily removed from the product gas by cooling. If nitrogen were used in a commercial application, it would be very costly to remove from the product gas.

The guidelines given by CANMET (194) can be revised as follows based on the above discussion:

Spent catalyst - 44 µm to 250 µm (some smaller sizes may be removed depending on fluidization tests)
- feed rate 175 - 1750 g/h
- bulk density 0.8 g/cm^3

Reactor size - 7 cm diameter by 85 cm high for 30 minute retention time with 1750 g/h catalyst rate

Solids retention time - 1 to 30 minutes

Fluidizing gas - Steam and oxygen - flow to be determined after fluidization tests and confirmation of reactor size

Reactor conditions - 600 - 1200°C
- Atmospheric pressure

Test duration - One shift, 5 - 6 h at steady state.

5.5.3 Feed and Product Systems

These systems will be essentially as described for the analogous system with the pyrolysis test unit in Section 5.4.4. It is important that uniform flows of spent catalyst and reactant gases be maintained to the fluidized bed to provide steady temperature control.

5.6 Process Development

5.6.1 State of Catalyst Development

The commercial configuration proposed for the pyrolysis/gasification process is the same as a fluidized catalytic cracking unit with catalyst flowing between the separate pyrolysis and gasification vessels. The unique aspect of the process outlined in CANMET's patent application (208) is the use of a bifunctional catalyst with active components for separately catalyzing both the pyrolysis and gasification reactions. Only a limited amount of work has been done to date by CANMET in developing a bifunctional catalyst. Some work has been done on the pyrolysis or gasification components individually but no bifunctional catalyst has yet been tested.

The only pyrolysis catalyst used by CANMET has been gamma alumina (62, 193). The use of this catalyst increased the yield of liquid products compared to pitch pyrolysis without a catalyst and improved the quality of the liquid product. There are, however, significant problems in applying gamma alumina to a bifunctional catalyst for pitch pyrolysis and gasification. These include:

- From fluid catalytic cracking experience (Section 3.3.2 (b)) it is known that impurities such as nickel, vanadium and nitrogen in the feed will poison active catalyst sites. The data in Section 4.0 show tha these impurities are present in high concentrations in most pitch feeds.

- The gamma alumina will transform to a catalytically inert form of alumina at temperatures in the range of proposed gasifier operation (193, 194, 201).

- Conventional catalytic cracking catalysts are known to deactivate beginning at 700 - 800°C (209). This effect is accelerated by the presence of steam with almost complete loss of activity occurring by 800°C.

The gasification catalysts tested by CANMET were potassium carbonate and vanadium pentoxide (156). In agreement with other workers they found that potassium carbonate enhanced the gasification rate while vanadium pentoxide inhibited it in comparison to non-catalytic gasification. Some of the concerns in applying a gasification catalyst in a bifunctional mode are:

- Potassium carbonate partially vaporizes at the gasifier temperature. The recovery and recycle of vapourized alkali metal catalyst was a key part of the development of Exxon's Catalytic Gasification process (Section 3.4.2 (b)).
- Vanadium will deposit on the catalyst during pyrolysis and then may act to retard the gasification reactions.
- The gasification catalyst may promote gasification reactions in the pyrolysis reactor which will downgrade the value of the gaseous products.

It is apparent that considerable development work remains to be done to prove the concept of the bifunctional catalyst.

5.6.2 Development Program

CANMET requested (194) that Hatch Associates not prepare a detailed development program for the process. There are, however, some general points that should be made.

The use of a bifunctional catalyst is the unique aspect of CANMET's pyrolysis/gasification reaction system. It is apparent from Section 5.6.1 that the state of bifunctional catalyst development must be substantially advanced before it can be confirmed as a viable concept. Hatch Associates feels that additional batch catalyst testing and development must be done to demonstrate a bifunctional catalyst before any further work is done to develop a more detailed design of the laboratory test units discussed in Sections 5.4 and 5.5.

As discussed in Section 5.4.2, basic fluidization testing with the proposed catalyst is required to determine its pressure drop, superficial velocity, bed expansion, bubble growth and bed mixing characteristics. This information is needed for design and operation of the laboratory test units.

Since a modular design is being proposed by CANMET, the pyrolysis reactor test unit should be constructed and tested before further work is done with the gasifier unit. This will allow confirmation that a fluidized bed pyrolysis unit can be operated without agglomerating and determination of the required solids:coke and solids:pitch feed ratios. These solids feed rates can then be used for the subsequent gasifier unit design. The measurement of the solids:pitch ratio will also confirm the process constraints between pyrolysis heat balance and reactor temperatures discussed in Section 5.4.3. If this is confirmed it will have implications for the concept of integrated pyrolysis and gasification reactors. Heat removal from the hot gasifier catalyst may be required either by use of a fluidized mixing vessel between the gasifier and pyrolysis units or by external heat exchange. The fluidized mixing vessel is analogous to the heater vessel used in Flexicoking.

Operation of the fluidized pyrolysis test unit should not begin with pitch feed since this represents its most difficult operating condition. The unit should instead begin with a gas oil feed where proven operation is known from fluid catalytic cracker operation. Once the components of the test unit have been proven on the gas oil feed, operation can be done with progressively heavier feeds, always starting at a high solids:pitch ratio. In this way the operation will approach the pitches that are most difficult to process in a controlled manner which will improve the chances of success.

The fluidized bed test units will provide information on reaction mechanisms and kinetics and allow development of bifunctional catalysts once the basic concept has been proven on a batch basis. Since the bifunctional catalyst is the unique aspect of CANMET's process, consideration should be given to collaborating with one of the Canadian researchers developing novel pyrolysis reactor designs discussed in Section 5.3.

5.6.3 Scaleup Considerations

The main purpose of the fluidized bed test units discussed in this report is to provide basic information on reaction kinetics and bifunctional catalysts. Because of their relatively small size, they will be only the first step in scaling the process to a commercial capacity. The hydrodynamics of gas-solids flow and contacting is quite different in small diameter, high L/D beds than in large diameter, moderate L/D beds. In a small diameter bed, the gas bubble growth is limited by the vessel diameter. As the bubble size approaches the bed diameter, it changes from a freely rising bubble to a slug which moves upward at a lower velocity than a bubble of the same volume. The gas-solids contacting and gas holdup time in slug flow are significantly greater than in bubbling flow. The solids and gas backmixing are less in high L/D laboratory beds than in lower L/D commercial reactor beds. These factors must all be considered in attempting to scale data obtained on a laboratory scale fluidized bed to a larger sized unit. The scaleup factors are expected to be different for the pyrolysis and gasification reactors.

The main factors in the pyrolysis fluidized bed are to provide good solids mixing for uniform dispersion for the pitch feed and to have adequate solids residence time for the residual pitch to pyrolyze. The product vapour should be removed from the bed quickly to minimize secondary pyrolysis reactions that will degrade the product yield and quality. A larger fluidized bed pyrolysis reactor would likely have a relatively low L/D and would be scaled-up on the basis of bed residence time and hydrodynamics for bed mixing.

In the gasification reactor, the contact between the fluidizing gas (steam, oxygen) and the solid (char, catalyst) is the important factor since they are the reactants in the gasification process. The small fluidized bed is a more efficient contactor of gas and solids as discussed in Section 5.5.1. Zenz has developed a correlation for the effectiveness of gas-solid contact (196, 198) that shows relative effects of bubble size, bubble velocity, bed depth, and the fluidization properties of the particle. This correlation can be used for scaleup by matching volumetrically integrated values of the contact effectiveness factor. Zenz has subsequently (210) used the contact effectiveness factor to develop a simpler procedure for an approximate scaleup based on gas-solid contacting.

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SECTION 6.0 - CONCLUSIONS AND RECOMMENDATIONS

6.0 CONCLUSIONS AND RECOMMENDATIONS

There are many processes for pitch consumption and conversion that are now being used commercially or are under development. Past studies have shown that none are clearly superior. It was found that a presentation of economic data for evaluating the processes on a consistent basis could not be done at the literature search level of accuracy. A more detailed general economic evaluation is not recommended since there are many application and case specific factors that affect the results.

Non-catalytic pyrolysis processes are being widely used with a variety of pitch feeds. Exxon's Dual Gasification Flexicoking process, though non-catalytic, is very similar in overall concept to CANMET's pitch pyrolysis/gasification process. Recent economic studies related to Athabasca bitumen or heavy oil processing have shown an advantage for hydrogen addition processes over non-catalytic pyrolysis processes.

Catalytic pyrolysis processes have not been widely applied to heavy pitch conversion because of problems with feed impurities and coke depositing on the catalyst. The catalytic pyrolysis work reported by CANMET has not taken any new directions that would avoid these problems.

Non-catalytic gasification is well proven commercially. Several process developers are working on catalytic gasification processes based on the use of alkali metal catalysts. The catalytic gasification work reported by CANMET has used similar alkali metal catalysts.

The unique aspect of the CANMET pyrolysis/gasification process is the use of a bifunctional catalyst with active components for catalyzing both pyrolysis and gasification. No bifunctional catalyst testing has yet been done by CANMET. It is recommended that additional catalyst development work be done on a batch scale to prove the bifunctional catalyst concept before any additional work is done on the continuous laboratory test unit.

Several reactor options were considered for the continuous laboratory test unit. A fluidized bed reactor was recommended for both pyrolysis and gasification because of its proven use in similar applications and its relative simplicity of operation. A riser reactor was not considered feasible with the 30 minute solids residence time specified by CANMET. Since several Canadian researchers are developing advanced pyrolysis reactors, it is recommended that CANMET consider collaborating with one of them by combining their catalyst technology with the new reactor system.

Basic fluidization testwork with the bifunctional catalyst must be done by CANMET before the design basis for the continuous laboratory test unit can be finalized.

It is recommended that operation of the continuous fluidized bed pyrolysis reactor begin with vacuum gas oil range feeds whose use has been proven in standard fluid catalytic cracking. This will allow the operation of the laboratory test unit to be proven before operation begins with progressively heavier pitch feeds.

Prior operation of fluidized beds with sticky feeds has shown that high catalyst or solids to feed or coke ratios will be necessary to avoid agglomeration. A heat balance of the pyrolysis reactor with a high solids feed rate showed that the catalyst entering the reactor had to be at a temperature about 100°C above the pyrolysis temperature. This is much lower than the temperature of the catalyst from the gasification reactor and suggests that integrated operation analogous to a fluid catalytic cracker may require catalyst cooling or an additional catalyst mixing vessel.

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SECTION 7.0 - REFERENCES

7.0 REFERENCES

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